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EFFECTS OF SPACE CHARGE IN POLYMERIC MATERIALS ON MECHANICAL AND ADHESIVE PROPERTIES

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*SELBY M. SKINNER
EDWARD L. KERN
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CASE INSTITUTE OF TECHNOLOGY

JANUARY 1958

WRIGHT AIR DEVELOPMENT CENTER

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AERONAUTICAL RESEARCH LABORATORY
CONTRACT NO. AF 33(616)-3400
WADC Task 70338
WADC Project 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report describes work done by Case Institute of Technology under Contract No. AF 33(616)-3400. Work is documented under Project No. 7340, "Rubber, Plastic, and Composite Materials," and Task No. 70338, "Effects of Chemical Constitution and Structure Upon the Physical Properties of Polymers."

In addition to the authors, there participated in the experimental work the following students of the Department of Chemistry and Chemical Engineering, Case Institute of Technology: George Eierman, Stephen Hinds, John R. Howell, Richard Jahnke, Oranda Kao, and L. Dale Smith. Discussion on various technical points with Professor E. G. Bobalek was of considerable value at certain stages of the investigation. The careful workmanship and contributions to design of apparatus by Mr. Herman Braun and Mr. John Stepka of the Chemistry Department Shop have been an integral part of the success of the apparatus which was constructed.

The Air Force scientist responsible for this task is Dr. P. M. Williamson of the Chemistry Research Branch, Aeronautical Research Laboratory.

ABSTRACT

The effects of space charge in polymeric materials on the mechanical and electrical properties of the materials have been investigated both theoretically and experimentally. The primary cause of space charge is contact of the polymer with other chemical materials, of which metals have been chosen as the chief example; within the polymer in the neighborhood of its contact with the metal a true volume charge of electricity exists which decreases in density with increasing distance from the metal. This charge can be positive or negative, and must be measured by nonequilibrium methods. The effects of different materials, different surface preparation of the metal, different polymerization schedules, heterogeneity in the metal and in the polymer, the presence of non-mobile charge in the polymer, have been studied theoretically and in detail experimentally utilizing a number of techniques developed especially to overcome the great sensitivity of surface or interfacial electrical measurements to traces of impurity or variation in composition.

The methods of measurement of the charge constituting the space charge are extended experimentally by use of electronic techniques, and vacuum conditions, and consideration is made of the effects of atmospheric discharge during the break of an adhesive bond. As in the previous report for polymethylmethacrylate, it is shown that a strong bond can be obtained with polystyrene under the proper experimental conditions. The use of the electrical potential trace at the break of the bond to study mechanical pulses and waves during the break is described. The chief content is, however, the theoretical and experimental investigation of the mechanical and electrical consequences of the space charge in the polymer; one of the most significant of these is the internal stresses which result when the charge content is such that the electrostatic component of adhesion is significant.

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SECTION I

INTRODUCTION*

In a number of fields of technology the methods in use are largely based on practical experience, survival of particular techniques which worked, and other "state of the art" procedures, none of which are susceptible to the type of precise explanation achievable with the phenomena used as examples in the physics, chemistry, or thermodynamics textbook. It is precisely this type of technique which must evolve in answer to the practical problem presented in the real workaday world; there results are primary, and time for investigation is often sharply limited. No one seriously doubts that the successful technique or methodology is successful just because it effectively utilizes basic chemical, physical, metallurgical, and other principles. The problem remains, how can the technique be extended and improved. In many cases, the barrier to improvement consists just in the fact that the number of chemical and physical factors which contribute to and affect the results obtained with a particular technique is so large that it is not possible to judge accurately the interplay of effects when deviating from the "tried and successful." In others, there may be involved the consequences of particular processes which have not been fully investigated. Typical examples of such fields of technology include those of surface preparation, organic coatings, adhesion technology, catalysis, reinforcement or molding of plastics or elastomers. Fields such as these are characterized by a wide body of scientific knowledge, but in their application, "state of the art" methods appear to a greater or less extent.

Under such circumstances, scientific investigation progresses in the fundamental scientific fields allied to the more practical profession or industry. Each new factor or phenomenon which can be identified and whose behavior can be understood contributes somewhat to reducing the complexity of the practical problem.

The present investigation represents the second part of an effort to isolate such a fugitive phenomenon, and study it on a fundamental scientific basis. As a scientific problem, it is of considerable fascination to the authors; the approach to its unraveling has required solid state theory, thermodynamics both classical and irreversible, electrostatic theory, certain portions of quantum theory, and the techniques of the polymer chemist and some of those of the surface chemist, together with suitable electronic circuitry. To the extent to which the results may also be of value in suggesting new ways of viewing old problems, and perhaps new methods of dealing with some of them, even at this early stage, some practical

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value may also be implied. However, as may easily be verified from the literature, the problems that remain to be answered in the general field, and some of which now occupy the attention of many investigators, far exceed those which have been undertaken by any investigators up to the present time.

It is common knowledge that the contact between different materials results in the transfer of charge between them; contact potentials between metals, the production of triboelectric charge by electrostatic machines or by the friction between shoe leather and a rug, the rubbing of glass rods with silk or hard rubber with cat's fur are common examples in the laboratory. In the previous report (WADC TR 56-158) it was shown that charge was normally to be found on plastic objects of considerable electrical resistivity, and that previously existent charge could be measured on broken adhesive surfaces.

Experimental results were obtained which implied that the charge was a volume charge distribution rather than being resident only on the surface if the material was sufficiently electrically resistant, and it was shown that a portion of the breaking force of an adhesive bond was force exerted to overcome the electrical attraction between adherend and adhesive which follows charge transfer between them. A detailed theoretical treatment using solid-state concepts and thermodynamics showed that both these effects were to be expected, although they are generally ignored in practice.

If charge does penetrate into the interior of plastic materials in the vicinity of an interface between the polymer and a metal, it will obviously affect the mechanical behavior and properties of the plastic. Also, the amount and distribution of such charge should be sensitive to the nature of the two materials on either side of the interface, and slight changes in chemical nature of either should produce differences in charge distribution and consequently in mechanical and electrical behavior.

The present investigation is a study by theoretical and experimental methods of the nature, distribution, and quantity of electrical charge which may be found in the interior of polymeric materials in the vicinity of metallic interfaces, and the types of mechanical and electrical effects which may result therefrom. It was the purpose of the investigation, as defined under the contract, to make a preliminary survey of the phenomena and the effects, and to consider in somewhat more detail only areas of such phenomena and effects in which it appeared that experimental effort would be likely to be productive.

The contents are self-explanatory, and nothing further than this report and standard textbooks is needed for following

the material therein. However, since the work is based on the theoretical development set forth in WADC TR 56-158, and reference is made to a number of the experimental results there described, it should be regarded as further extending the work of that report.

SECTION II.

THEORETICAL BACKGROUND.A. Application of Solid State and Thermodynamic Concepts to the Electrical Phenomena in Plastics and other Insulators.

1. History.

In a previous Technical Report (36), and in a number of articles (37-41, 45), the present author has advanced and developed the concept that the electrical behavior of insulators, and especially of plastic materials, is describable by solid state concepts, in such a way as to agree with the requirements of thermodynamics. From this development, the static charging of insulators, the current flow through insulators and semiconductors, and the overall thermodynamic equilibrium follow, and such quantities as the conductivity of a given material, the difference in charging behavior of different types of materials when placed against a given substance, and the nature of the equilibrium of charged carriers free to diffuse but obeying the forces due to the electromagnetic field, are described in ways agreeing with experiment. From the development, there emerges the result that at an interface between two different materials, there is to be expected a transfer of charge which renders one material positive, the other negative, and results in a double layer in the vicinity of the interface. In an insulator, this double layer is the zero current space charge limit of the phenomena responsible for rectification at dielectric contacts, and represents the behavior of the electron atmosphere. It exists whether or not one or both of the materials are metals (as in contact potential phenomena), or whether they are one or both semiconductors or insulators.

The theory was developed for insulators, and as at present developed, applies strictly only to insulators, and materials with a sufficiently large intrinsic energy gap between the conduction and the valence energy levels so that it is not necessary to consider the contribution of more than one type of carrier to the flow of current through the substance. It predicts that the portion of the double layer at a metal-insulator contact which lies within the insulator is not confined to the surface, as is the case in a metal; instead, the charge extends throughout the material, so that equilibrium is a state of volume charge in the insulator. The charge density decreases in the insulator with increase of distance from the interface, and at finite distances from the interface, the charge density may be neglected. However, its existence is responsible for the difficulty in removing undesirable electrostatic effects from insulators, such as plastics, by process of surface destaticization. A destaticizer applied to an insulator will affect the surface only, and is subject to later removal by processes such as washing or rubbing, whereupon the contained volume charge in the insulator becomes again evident.

From the existence of a charge separation at an interface, it also follows that the transfer of charge results in a force of attraction between the two materials which is due entirely to electrostatic forces. This "electrostatic component of adhesion" was derived and described in full in the previous technical report (36), for the various particular cases. A number

of experiments were there described which gave indication of the actual physical existence of the electrostatic component of adhesion, and which measured the portion of the charge which could be measured under the physical conditions, and compared the thereby computed force to the actual breaking strength of the adhesion samples. Generally, it was found that the predicted force increased with the actual breaking strength, in many cases linearly over a large range; because of difficulty of measuring the actual charge remaining after the break of an adhesive bond, this actual charge was smaller than was expected, and the electrostatic component of adhesion, while shown to be real and existent, was nevertheless apparently only a small fraction of the total breaking strength.

While the possibility of charge transfer between nonmetals has long been known, and often demonstrated experimentally, it has been regarded essentially as a triboelectric phenomenon, and the rubbing of, for example, silk and a glass rod, has been viewed as the cause of the separation of charge. More lately, the view has begun to be accepted, that the rubbing achieves primarily intimate physical contact between the two substances, and that the charge transfer is a natural result of this close contact (20, 12, 13, 30). An adhesion bond is usually prepared in such a way as to achieve such intimate contact between polymer adhesive and metal adherend, and therefore has furnished a suitable experimental medium for investigation of both the fundamental factors involved, and the practical consequences in technology.

2. Phenomena.

The question of adhesion forces is only one of the technological consequences of the electrostatic charge separation at the junction between dissimilar materials. Some others are described below. In the investigation of any of these, it must be remembered that electrostatic measurements have usually, in the past, been regarded as "wild variable" experiments; the nature, quantity, and behavior of electric charges depend so much upon accidental minute changes in experimental conditions, that apparently identical experimental techniques and preparations have generally failed to give consistent results, and attempts to identify and remove the causes of the large variations observed have usually been unsuccessful.

In part, the cause is the transitory nature of any electrostatic condition. If the experimental phenomenon is a nonequilibrium such as a separated small charge, it rapidly disappears as equilibrium is approached. If, on the other hand, it is an equilibrium condition, one of two experiences present themselves: either the charge observed at equilibrium is so small that measurements are difficult, or the equilibrium is continually being disturbed by minute change of chemical environment or by the access of energy. Thus, in the first case, there is a general tendency for strong fields to be neutralized by selective attraction of ionized particles, polar materials, or other e. g. chemical effects, and local neutralization occurs rapidly. In the second, wandering dust particles, foreign atoms, and even local fluctuations of gaseous environment occur continually, and such factors as temperature change, radiant energy reception, and, in some cases, the effects of mechanical forces, may change the overall phenomena. The effects are all related to the fact that electrical charges obey long rather than short range forces. Very great experimental precautions are therefore necessary. It may also be observed, that a number of other phenomena show similar transitory existence: for example, a pair of freshly drawn

glass filaments will adhere strongly when one is pulled over the other, whereas they show little, if any, adhesion after being exposed to the air for several hours.

A number of experimental phenomena are known which are analogous to the interfacial effects studied in this report. A list of some of them follows:

(1) Charging of plastics during molding. Woodland and Ziegler (51) showed that plastic wall tiles acquired electrical charges which were responsible for the attraction of dust particles and therefore the discoloration of the tiles in use, and that these charges were acquired during molding, and no charge was obtained on portions which did not touch metal parts during molding.

(2) Russel effect. A freshly abraded metal surface applied immediately to a photographic emulsion will "expose" the emulsion in the dark, and upon development, the image appears of the regions at which the metal touched the emulsion. (4) (5)

(3) Metal which is machined under water results in a concentration of hydrogen peroxide in the water related (quantitatively, in one case) to the number of fresh atoms exposed during the machining. The same metal machined just above the water, with chips dropping into the water, results in a considerably smaller quantity of hydrogen peroxide.

(4) Polymer which is polymerized in a glass vessel, shows flashes of light associated with electron discharge, at the time of its breaking away from the glass because of shrinkage. (5)

(5) Kramer effect. A freshly abraded metal surface itself emits (or causes a reaction in which there are emitted) electrons which can be measured with a Geiger counter. (24)

(6) Long range electrons of kilovolt energy are detected at the breaking of an adhesion bond. (23)

(7) Schurmann effect. Stick-slip phenomena in boundary lubrication, of metal sliding on metal or nonmetal, are accompanied by electrostatic discharges. (35) (40)

(8) The surface tension of mercury varies with applied electrical potential, the phenomenon of electrocapillarity. (5) (1) (3)

(9) Johnsen-Rahbeck effect. When a potential is applied between a semiconductor and a metallic plate in contact with it, there is a strong force of attraction between the two. The cohesive (sic) force between the two is proportional to the square of the potential difference, and is attributed to the electrical field in the small air spaces at regions of noncontact. (22) (2)

(10) The viscosity of a polar material increases when an electrical field is applied perpendicular to the direction of flow of the fluid. (46)

These and many other types of behavior of materials show the importance of the effects of electrical charge distributions in materials. The present investigation was entered upon primarily to obtain further information upon the effects of contained charge upon adhesion, and upon the mechanical properties of polymeric materials.

Polymers and ceramics, particularly those of high insulating value, have been particularly useful to the electrical industry. As a result of continued manufacture and use over the years, a continually improved product has been obtained. In electrical usage, it has been necessary to develop materials of high electrical resistance, low loss factor (energy dissipation), and high electrical breakdown strength. The high resistance insures a large intrinsic energy gap, the low loss factor and high breakdown strength imply a minimum of internal cracks, imperfections, or polarity, all of which would increase either the Maxwell-Wagner loss, or the Debye absorption. Therefore commercial plastic materials intended for electrical use (and similarly, ceramic materials) may be regarded as homogeneous electrically with a minimum of donor or acceptor levels, and with a forbidden (intrinsic) energy gap of from two to seven eV. With such materials, much of what is shown in the succeeding text may easily be at least qualitatively observed in technology. Less homogeneous materials, or less resistant materials show the same phenomena to a smaller extent, and some of the effects of the inhomogeneity may mask certain of them. However, in order to increase as much as possible the degree of accuracy obtainable in experiments, it was necessary here to develop techniques of preparing especially pure and homogeneous polymers under reproducible conditions.

3. Basic Concepts.

The basic solid state and thermodynamic concepts which have been applied by us to the charge behavior of polymers have been described in detail already (34, 36, 37, 38, 44, 49). Here they will merely be sketched.

It is assumed that charges in an insulator are either bound or free. The bound charges are characterized by an energy equal to or less than the characteristic valence energy level, Fig. 1. The free charges result from a thermal equilibrium; since the forbidden (or intrinsic) energy gap which exists between the valence level and the conduction level is large, there are very few conduction electrons. Their number is given by $n = N_c \exp(\epsilon_c - \epsilon_f)/kT$, (1) where ϵ_f is the energy of the Fermi level (essentially the free energy per particle), and is equal to or less than the energy of the conduction electron. The Fermi level in an uncharged insulator lies about halfway between the conduction and the valence level, so that the quantity in parentheses in this expression is about half the intrinsic energy gap, $E_i = (\epsilon_c - \epsilon_v)$. (2) (3)

$N_c = 2(2\pi mkT h^{-2})^{3/2}$

and is the partition function for translatory degrees of freedom, since these are the only ones appropriate to electrical charges, i. e. electrons (or holes). The remainder of the expression is the Boltzmann factor describing the reduction of the number of carriers with increasing energy which is characteristic of thermal equilibrium. Obviously, only classical densities of electrons are in question, since the Boltzmann expression is not valid in the case of electron

degeneracy; however, since the materials in question are of high resistance,

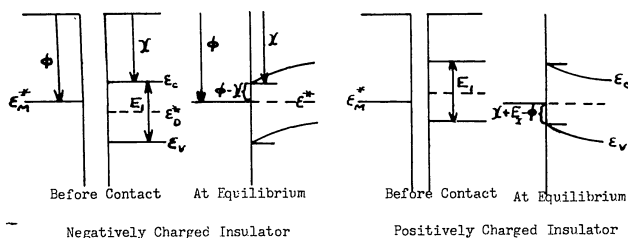


Figure 1

the intrinsic energy gap is large, and therefore the number of free charges is small.

Upon contact with dissimilar materials, the polymer is charged either positively or negatively, since, in general, the Fermi levels in the two materials will not be the same. The flow of charge from the material of higher Fermi level into that of lower level renders the latter negatively charged, and the former positively charged. Simultaneously, the Fermi level rises in the negatively charged material, and is lowered in the other, until finally equilibrium is reached when they are both at the same level. In general, the final state is one in which the Fermi level is no longer midway between the conduction and the valence levels; however, in a metal, the change in height of the Fermi level is negligible because of the large concentration of free electrons which characterizes a metal.

The equilibrium state after contact between two dissimilar materials, of which one is a polymer and the other a metal, therefore finds the Fermi level of both materials nearer to the conduction or the valence level of the polymer than it was originally. Therefore the concentration of charge (electrons in the conduction level, or holes in the valence level) is greater than when it is not in contact with another substance. Since the mathematical description of the two cases is nearly identical, the case of additional electrons in the conduction level is chosen for discussion. In this case, the Fermi level is nearer to the conduction level than before contact, and the density of electrons in the polymer at the boundary is

$$n = N \exp \left[\frac{E_c - E_f}{kT} \right] \quad (4)$$

where E_f is the new position of the Fermi level, as shown in the previous report.

Within the polymer, however, another factor enters, namely space charge. After some charge has diffused into the polymer, succeeding charge must overcome the repulsion of the charge already in the polymer in order to penetrate towards

the interior. The energy necessary for an electron to continue to diffuse as a free charge therefore increases towards the interior, and by the Boltzmann expression, the number of electrons per unit volume which can diffuse to a given depth decreases accordingly, at greater and greater depths within the dielectric. The charge density, and the potential finally establish themselves at levels which depend upon the distance, the boundary conditions, and the total quantity of charge in question, as described mathematically in ref. 37. The final state is a thermal diffusion equilibrium including the effects of the electrical field. With the usual values of total charge transferred, the excess charge density because of interfacial conditions becomes negligible at distances of the order of 10^{-4} cm or less; therefore the insulator still remains an insulator. With very thin films, however, greater electrical conductivity than for the bulk material may be expected; this has been observed, and is predicted, for example by the theory of Mott and Gurney (30,46) as well as the present treatment.

The existence of a volume charge in the insulator and the opposite charge on the metal results in an electrical attraction between the two which may be described by the usual electrostatic expressions, namely $f = (e/8\pi) F^2$, where f is the force (of attraction towards the metal) per square centimeter at any point within the polymer, and F is the electrical field at that point resulting from the contained charge. At the interfacial boundary, this force becomes the total adhesive force which is due to electrostatic effects, and in the case of an insulator whose thickness is large compared to a characteristic distance x_0 , this adhesion is given by $f = n_0 kT$, where n_0 is the limit of the charge density in the polymer as the interface is approached from within the polymer. The characteristic distance x_0 is given by $x_0^2 = \epsilon kT / 2e^2 n_0$, and therefore is determined by the experimental and boundary conditions. The total charge transferred through unit area of the polymer during the establishment of equilibrium is, in this case, $q = n_0 x_0$.

The discussion above has dealt with the basic concepts in a highly qualitative manner. For the detailed mathematical development, the previous technical report and the other references should be consulted. Results from them will be used in the text below without further development, merely by reference to the appropriate page and publication.

4. The Electrochemical Potential.

The electrochemical potential is the sum of the electrical potential, and the chemical potential. By the development, this is $U = \psi + kT \ln(n)$, where each term is an energy, e. g. electrostatic potential times charge. In all three cases which result from the mathematical development, this quantity is independent of distance, i. e. of the location within the polymer. This does not mean that the individual electrical and chemical potentials are constant in the polymer, but that the change of either as the interface is departed from towards the interior of the polymer is the negative of the change of the other, so that their sum is constant. This is a thermodynamic requirement, of course, since the gradient of the electrochemical potential is proportional to the total current flowing through the insulator, and the equilibrium case under consideration is a static one, i. e. of no current flow.

The reason for the constancy of U , phenomenologically, however, is interesting in itself, since it agrees with the space charge requirements of electrostatics. As the electrical potential increases towards the interior of the polymer because of the space charge, so does the number of electrons decrease, which can diffuse freely up to that potential. The higher electrostatic potential automatically selects only those electrons from the metal which have energy sufficient to overcome this higher barrier to diffusion. Since the electrons in question are those in the metal which have attained energy greater than the Fermi energy because of thermal equilibrium at temperatures higher than zero, their number decreases as only those with increased energy are taken into consideration. The decrease is just sufficient to cause the factor " $kT \ln(n)$ " to decrease by the same amount that the electrostatic potential increased because of space charge.

This is true whether the polymer is of infinite or finite extent, in contact with a metal at one interface or at two separated interfaces, or in contact with different metals. It corresponds with the fact that the electrochemical potential differs from the Fermi energy only by a constant, and therefore is a thermodynamic function which must be constant in equilibrium.

B. Extensions of the Concepts Previously Developed.

1. Heterogeneity.

If consideration is restricted to insulators, there are two major directions in which the theoretical considerations should be extended. The first is that of making provision for the effect of heterogeneity in composition, and the second, that of considering the possibility of the existence of trapped charges, whose electrostatic field will affect the distribution of the free charges. In the latter, carried to the limit, appears the concept of surface charge.

The effect of heterogeneity of composition may be illustrated by the simple case of two different dielectrics in contact over an interface, each being bounded on its other side by a metal. Since the experimental arrangements will be of finite thickness, the finite solution is appropriate, and suitable boundary conditions must be applied to each dielectric. The results are given in detail in Appendix I.

2. Bound Charge.

The effect of contained bound (trapped) space charge is treated in Appendix II. It is sufficient here to say that such bound space charge of the same sign has the effect of moving the center of gravity of the charge distribution in the polymer nearer to the interface. In the planar case, where all quantities are independent of y and z coordinates, this produces little change in the value of the electrostatic component of adhesion, the effect being merely that of reducing end effects at the edge of the adhesion sample. In the fields from curved surfaces, the effect can be considerably greater. If there were no end effects, the lines of force would all be parallel to each other, and the effect at the boundary would be the same force on the metal component, whether the charge were near the interface or distributed in the space beyond it. Thus, even in the extreme case of a charge residing entirely upon the surface, the electrostatic force would be $f = 2\pi q^2 = 2\pi(n_0 e x_0)^2 = n_0 kT$, as

before, where n_0 is now not the actual volume charge density at the surface, but the charge density at the surface which corresponds to a thermodynamic equilibrium distribution of a total amount of charge equal to the actual existing surface charge density.

On the other hand, the electrical force urging the polymer toward the metal, as it would be observed not at the interface, but some distance within the interior of the polymer does depend upon the distribution of charge, and is decreased the more nearly the charge approaches the interface.

3. Trapped Charge.

The question of donor and acceptor levels which are partially filled, and whose equilibrium is a thermodynamic one, has been treated elsewhere (43). It yields results similar to those for free charge except for a new definition of the dielectric constant. The consequences of such considerations are considered in the text below.

4. Cohesion and Adhesion.

Within the polymer, there must be forces of cohesion. Even if this were not obvious on other physical grounds, it would merely be necessary to consider the adhesive bond consisting of a polymer layer between two identical metal adherends. The electrostatic solution shows that in the center of this combination, there is a small charge density, but no electric field, i. e. that there is no electrostatic force urging the material in either direction. Without cohesive forces, the material would fall apart at this plane, at least. Actually, the adhesive force as computed by the relations developed, is a maximum at the interface and decreases towards the center of the adhesive layer; cohesive forces within the material are responsible for the holding together of the layer, and within the material there must be a gradual transition from adhesive to cohesive forces in the force train from one adherend to the other.

The adhesive force can also be regarded as an internal pressure pushing the polymer toward the metal. Because of the space charge effect, this force increases towards the interface and at the interface becomes the electrostatic force of adhesion, balanced by exactly the same value of force urging the metal towards the polymer. Both phenomenologically and mathematically this view is consistent. One of the effects of such a pressure is to place the interior of the polymer under an internal pressure which constitutes a stress. In the vicinity of the metal, the cohesive forces must be great enough to compensate for this internal stress.

During the breaking of an adhesive bond, a stress is applied externally to separate the halves of the adhesive bond. If there is an internal stress already existent in the polymer which is attempting to do the same thing, the actual breaking stresses experienced by the polymer are greater than if there is no such internal stress. Thus, the measured tensile strength of a specimen of the material would be expected to be smaller if there exists a charge within it; such an effect has been observed (17).

In the vicinity of the interface, therefore, remembering that no surface is truly planar, it is quite possible that stress conditions at break would be such as to favor break at other than the exact interface. Thus a

metal adherend may be expected to retain portions of the adhesive in subvisible quantities, or if weak points exist in the polymer, may even take with it macroscopic quantities of polymer. The conditions at the exact interface (if such exists) may actually be very difficult to describe, and the transition from polymer to metal may involve such charge and field distribution changes as to favor break just within the polymer.

However, there is sufficient indication that increase in adhesion may be accompanied by decrease in cohesion, that it is possible to state that it is likely that the strongest bond attainable with given adhesive and adherends will show a proper balance between adhesive and cohesive forces, and that alteration of preparational technique in either direction away from this balance will decrease the measured strength of the bond; in one direction, cohesive failure is observed, and in the other adhesive failure.

C. Lateral Forces Accompanying Charge Distributions.

The adhesive force at the boundary of the dielectric adhesive which has been described in ref. 36, is the component of the Maxwell electrostatic stress system which lies along the direction of the electric field. The components of this stress are given by

$$\left. \begin{aligned} 8\pi e^2 X_x &= \left[\left(\frac{\partial \psi}{\partial x} \right)^2 - \left(\frac{\partial \psi}{\partial y} \right)^2 - \left(\frac{\partial \psi}{\partial z} \right)^2 \right] \epsilon \\ 8\pi e^2 X_y &= \left[\left(\frac{\partial \psi}{\partial x} \right)^2 + \left(\frac{\partial \psi}{\partial y} \right)^2 - \left(\frac{\partial \psi}{\partial z} \right)^2 \right] \epsilon \\ 8\pi e^2 X_z &= \left[\left(\frac{\partial \psi}{\partial x} \right)^2 - \left(\frac{\partial \psi}{\partial y} \right)^2 + \left(\frac{\partial \psi}{\partial z} \right)^2 \right] \epsilon \\ 4\pi e^2 X_y &= \left(\frac{\partial \psi}{\partial x} \right) \left(\frac{\partial \psi}{\partial y} \right) \epsilon \\ 4\pi e^2 X_z &= \left(\frac{\partial \psi}{\partial x} \right) \left(\frac{\partial \psi}{\partial z} \right) \epsilon \\ 4\pi e^2 X_x &= \left(\frac{\partial \psi}{\partial y} \right) \left(\frac{\partial \psi}{\partial z} \right) \epsilon \end{aligned} \right\} \quad (6)$$

If this is formulated in a coordinate system which takes the axis of x parallel to the normal of the electrical equipotential surface at the point, it may be shown that the stress (traction) across the equipotential surface at the point is given by $f = \frac{E^2}{8\pi}$ where $E^2 = \left(\frac{\partial \psi}{\partial x} \right)^2 + \left(\frac{\partial \psi}{\partial y} \right)^2 + \left(\frac{\partial \psi}{\partial z} \right)^2$ (7)

i. e. the stress is the square of the resultant electrical field in electrostatic units, divided by 8π . Similarly, the stress in any plane perpendicular to the equipotential plane is a pressure of the same magnitude.

In the case under consideration, therefore, there is a mechanical force of adhesion at the dielectric interface, and within the dielectric material, a force in the same direction (the x direction) which becomes smaller towards the interior of the material. Also, there is a lateral pressure (perpendicular to the direction of the electrical field i. e., in any direction in the y, z , plane) attributable to the mutual charge repulsion, which, at any point, is identical in magnitude with the mechanical force directed along the field. Such a system of internal stress implies a certain amount of internal strain, and requires body forces for its equilibration (28). In the adhesive bond, the equilibration longitudinally is supplied by the stress from the opposite

surface charge on the metal adherend, and from any molecular or Van der Waals forces. The equilibration laterally is supplied by the internal forces resulting from the strain, i. e. forces of the nature of cohesion.

The effects of such lateral forces must also be considered in the analysis of the effects upon polymeric materials of charge distributions within them.

D. Possibilities for Test or Confirmation of the Theory.

1. The Nature of Equilibrium.

At equilibrium, the charges will have, so far as possible brought to them opposite charges, and, even where space charge exists, the potential and charge behavior results in a constant electrochemical potential. Therefore, just as in the measurement of contact potentials in metallic circuits, observable effects have disappeared.

2. Use of Nonequilibrium Effects.

The traditional method of observing contact potentials between metals is to touch and separate the metals and observe the charge or potential resulting from the charge transfer at contact. This is a nonequilibrium type of experiment. The breaking of an adhesive bond is a similar type of nonequilibrium effect. Other types of nonequilibrium effects have been considered, and as indicated in the previous report, the behavior of current vs. applied voltage seemed to offer possibilities for the study of the present effects. However, as a measurement tool, this behavior is not useful because of length of time before steady state conditions are attained and the many other effects which accompany such an experiment.

A number of the phenomena listed in Sec. II, A, 1, offer possibilities for this purpose. However, the techniques which have been developed by the surface chemist, and in adhesives technology, offer more promise of freedom from "wild variable" behavior than any of the other types of experiment which were considered. Qualitative observation of some of these phenomena have been undertaken, and reported in the progress reports of this contract, but, where the results have been inconclusive, their description has usually been omitted in the text below.

SECTION III

EXPERIMENTAL APPARATUS AND TECHNIQUES.

A. Mechanical Measuring System.

1. Baldwin - Tate Emery Tensile Test Machine.

A Baldwin Tate Emery Model MTE - 5 Tensile Testing Machine, Fig. 33, was used for the mechanical testing. This applies desired constant rates of elongation from 0.03 inch/min to 20"/min to the sample, with dial indication of the stress, and a maximum stress indication at break. There was available automatic recording of stress vs. time; a specially constructed addition to the machine was also available involving a number of individual motors and an additional recording pen which permitted strain vs. time measurements to be determined by a separate record, by means of square-wave pulses initiated by an operator who followed the extension of the test specimen with scale. The latter was only used during the testing of the mechanical properties of the bulk polymer.

The machine was freshly calibrated shortly after the commencement of the experiments described in the text. It was used for most of the work, especially because of the small amount of backlash in strain measurements. The machine was located in an air-conditioned, constant temperature, constant humidity, room, designed particularly for ASTM conditions, but permitting variations from these temperatures and humidities.

Some attempt was made to bring the room down to very low humidities. The cooling system had not been designed for this purpose, and at very low humidities, it was necessary to take out so much water from the atmosphere that the cooling coils would freeze over, and undesirable temperature cycling would commence. Therefore low humidity and low pressure experiments were performed in a specially constructed separate small enclosed volume surrounding the specimen.

Experiments made with specimens in these specially designed containers with dried air at pressures down to 0.01 or 0.005 mm Hg. showed little difference in the types of electrical traces obtained, and, therefore, except for the experiments performed under vacuum, no attempt was made to alter the humidity from the 50% level. Separate experiments performed under vacuum showed that in the case of metal-polymer contacts, a lower pressure than that just mentioned is necessary to produce characteristic changes in trace pattern. The ones obtained are characteristic of the behavior of adhesive bonds broken under the usual conditions in practice.

2. Instron Tensile Test Machine.

In a portion of the work there was available an Instron Tensile Tester, Model TT-C, with automatic recording and controls. With this machine there was used a Sanborn Model 150 Multichannel Recorder for detailed recording of tensile data. The Instron was in a separate, newly constructed constant temperature, constant humidity, room. It was freshly installed, calibrated, and adjusted.

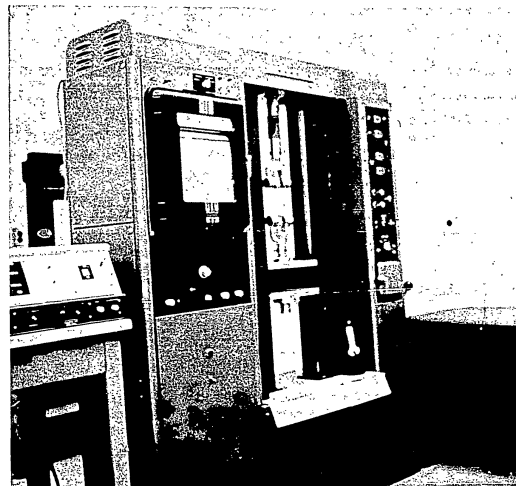


Fig. 2. Instron Tensile Testing Machine and integrator for the energy during a rupture.

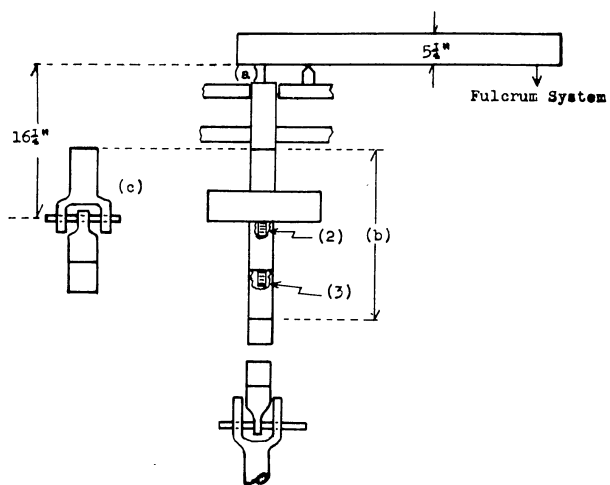


Fig. 3

Mechanical Measuring System Using
a Baldwin Tate Emery Tensile Machine.

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3. Mechanical Construction of Measuring System on the Baldwin - Tate Emery Tensile Test Machine.

In another section (Sec. XVII), the study of instantaneous shock waves and pulses by the electrical discharge at break of an adhesive sample is described. In connection with this, it is necessary to know certain mechanical details of the Baldwin - Tate Emery machine.

The stress is applied to the specimen through a mechanical system shown in Fig. 3. Since speed of separation of the jaws is constant, the stress varies according to the nature of the specimen and the time. This stress is measured by the dial gage, through a series of mechanical levers and beams, the actual determining link being a small lever in which the indicator of the applied stress is balanced against the force applied to it by a constant air flow. In the figure showing the mechanical system, dimensions are given, from which it is possible to determine, at least roughly, the times of travel of impulses in the system. These are discussed further in Sec. XVII and Appendix IV.

B. Electrical Circuitry and Apparatus.

1. Measurement of Charge Pattern at Break.

For this measurement, there is necessary an oscillograph with recording camera, which: 1) will not fog the film while it is being exposed to the oscillograph face during the rather long (up to a minute) and indeterminate period which elapses between the initial application of force to the specimen, and the actual break; 2) will record the whole trace upon the occurrence of the break; 3) preferably will do so whether the trace is a positive or a negative trace, so that half of the prepared samples are not lost; 4) will not distort the trace, in so far as this is possible; 5) has a maximum sensitivity in so far as this is consistent with freedom from background.

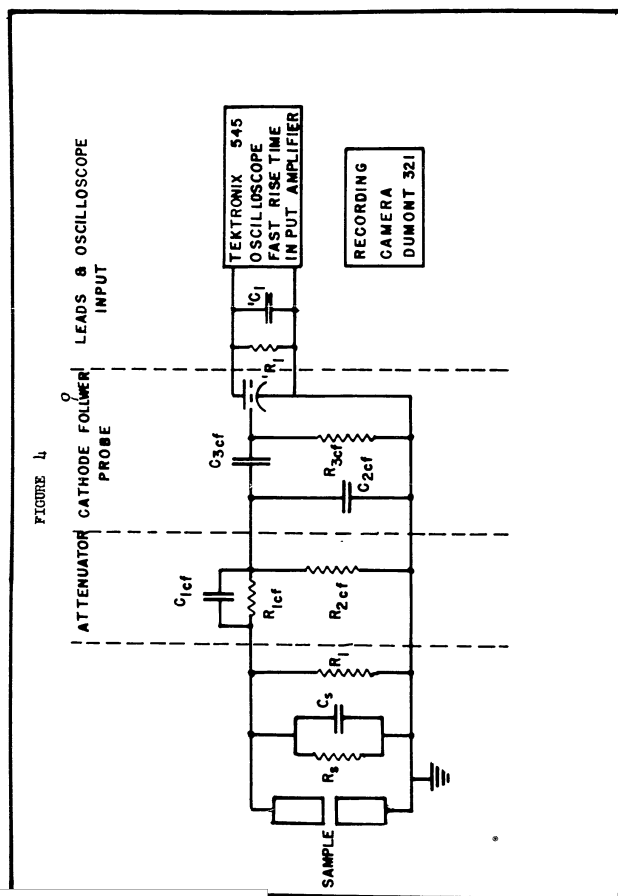
These requirements add up to the necessity for a triggering circuit which can use the actual break as a trigger, a time delay so that the electrical signal does not reach the deflection plates before the sweep has started, the ability to trigger on a pulse in either direction, and preferably a circuit which will show a second trace if the trace has not descended to zero at the end of the first sweep. Not all these, together with freedom from noise could be obtained in one instrument. However, a Tektronix 545 oscilloscope properly set supplied all of them except triggering on either sign pulse. It was used for most of the work described here. To accomplish the triggering on either sign, a special external triggering circuit was constructed which would accept either sign of pulse and generate an output positive pulse. About the same time that this was successfully completed, it became unnecessary, since it was discovered how to obtain preferential stripping of adhesive from the desired surface, so that connections could be made to give the desired sign pulse every time. A Dumont 323 was also used; its rise time was somewhat slower, but it permitted triggering on either sign, and would show repetitions. After the sample preparational technique had developed to the point at which it was possible to obtain break from one predetermined surface, triggering on a single sign pulse only, was satisfactory and the Tektronix oscilloscope was chiefly used.

Resistances across the samples were of 1% accuracy.

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2. Oscilloscope Circuit.

This is shown in Fig. 4. The signal was applied either to the input, or directly to the deflection plates on the DuMont. On the Tektronix, it was applied to the input, and amplified according to the sensitivity necessary. In order to decrease the electrical distance between sample and oscilloscope, a P170CF cathode follower probe was used (Fig. 4 shows a typical cathode follower circuit), and for a considerable portion of the work a P110 attenuator probe. These are described in the literature.

The original cathode follower gave trouble because of sensitivity of the vacuum tube to microphonics; this is particularly so, when it must be mounted on a specimen which is being stressed and broken. A flexible mounting overcame the microphonic sensitivity, and permitted satisfactory operation. The cathode follower circuit was discarded after several months' working with it, as sufficient sensitivity to the trace pattern could be obtained without it, and its operation made the analysis of the resulting trace for the integral charge more difficult.

Extensive testing of the oscillograph and circuit with pulse generators showed that the input and output signal corresponded closely when the ten times attenuator probe was used without the cathode follower. The 5K/54K fast rise time preamplifier in the 545 has a rise time of .006 usec. Therefore the entire characteristics of the pulse shape are determined by the sample behavior and external circuit.

3. Ballistic Galvanometer.

Some work was done with a ballistic galvanometer, but this was not considered suitable, since the pulse frequently had both positive and negative components, and it was necessary to consider each one separately in the analysis.

C. Measurement of Mechanical Phenomena Occurring at the Tensile Break of an Adhesion Specimen.

1. Strain Gage Recordings.

Some work was done with strain gages, to measure the mechanical behavior just before and during break. This was found unsatisfactory, since the break of an adhesion sample does not occur by uniform motion of a sample in one direction. The data from one or two strain gages does not yield a true picture of the break.

2. Mechanical Pulses and Waves.

In the work described in Sec. XVII, it was desired to isolate the mechanical phenomena for study. In order to do this, special shapes of metal were machined, which would serve as reflectors of pulses or waves originating in the shock of break. These are shown in Figs. 24-32. The pulse leaving the specimen would be reflected and arrive back at the sample at a time determined by its speed of travel in the metal material, and the geometry of the support. The analysis of the results follows from the dimensions of the special supports and of the tensile test machine. Attempts to initiate break by a superimposed shock wave when the specimen was in tension and near its probable breaking strength were not sufficiently precise for accurate calculations; the shock was

never a clear and precise pulse or wave, and the nature of the break initiated by the shock, when it occurred, depended upon more erratic local parting of the adhesive than desirable.

D. Other Apparatus and Techniques.

Other special apparatus and techniques, including the Faraday ice pail, the capacitometer, the method of determining charge distribution on the broken sample after break by powder patterns, etc. have been described in the earlier report.

In succeeding sections, there are discussed in detail the various special techniques which were developed for the purposes of this project. These had as their primary purpose the production of such uniform materials, preparational techniques, and subsequent handling as to decrease as much as possible the wild variability which has, in the past, been characteristic of measurements in the electrostatic field. They yielded therefore additional information in the mechanical and chemical field.

SECTION IV

METAL SURFACE PREPARATION AND ITS EFFECT ON MEASURED ADHESION

A. Metal Surfaces and Materials.

1. Surface Effects.

It is well known that the work function of a surface depends upon the history of its preparation. Small amounts of adsorbed chemicals, differences in crystal faces, the chemical and mechanical processes which have acted upon the surface change its surface free energy. Similar effects may be observed with respect to the activity of catalysts. Different surface preparation of the same metal affects its passivity, and the degree of adhesion to it which may be obtained with a given adhesive.

In the earlier experiments, ref. 36, there was developed a particular, accurately reproducible, surface preparational treatment, which permitted measurement of surface charges with considerably greater precision than in the usual adhesion technology, and gave strong adhesion between metal and polymer. It was here desired to study other methods of surface preparation, and determine the effect of these methods upon the breaking strength, and the manner of separation of adhesive and adherend. Primarily, this was in order to obtain a method of preparation which would permit preferential stripping at one interface, under reproducible conditions. The data were also considered with respect to possible later correlation of the surface preparational method with the observed charge on break. The effect of metal surface preparation on breaking strength of otherwise identically prepared specimens was sufficiently great to be of interest for itself.

2. Metal Specimens.

Commercial high purity copper and aluminum samples conforming to ASTM Standard D897-49, approximately 1.16 inch in diameter (described in WADC Technical Report 56-158) were used in the earlier portion of this work, during which the question of breaking strength vs. polymer thickness was also investigated without conclusive results. From the results, it became evident that a smaller surface was necessary to aid in minimizing or eliminating scratches during grinding, to permit better handling in the preparation of adhesion samples, and to minimize the flexural component on the specimen during the tensile stressing of the samples. Half inch diameter samples of 99.9% pure aluminum (99.99%), copper (99.9% assay), and nickel (99.99%) were machined, and given the surface treatments outlined below. The specimen is circular-cylindrical, 3/4 inch long, with a 3/8 inch threaded concentric hole bored into it for attachment to the tensile tester. Samples smaller than this would introduce too great edge effects from oxidation or other factors around the rim, and larger ones would be subject to greater likelihood of inhomogeneity over the surface.

with alumina slurry on glass. Buffing was done in one direction only with 3-0 paper supported by a glass plate, followed by similar buffing with 4-0 paper in the perpendicular direction. This leaves tiny scratches in the surface.

C. Correlation with Breaking Strengths.

1. Effect of Grinding for an Unoxidized Surface.

The effect of grinding for elimination of the oxide layer is shown in the following results for aluminum samples with polymethylmethacrylate adhesive.

Table I.

Effect of Oxide Layer on Breaking Strength.
Aluminum Samples-Polymethylmethacrylate.

Method	Breaking Strength, psi
Both surfaces ground under water	128±27
Both surfaces ground under toluene	217±37
One ground under water, other under toluene	73±9

2. Breaking Strengths as Correlated to Type of Surface Treatment.

The effects of differences in surface treatment can only be determined with confidence if all other factors are maintained as nearly as possible constant. For this purpose, the painstaking technique described elsewhere in this report was developed, requiring from two to three weeks of continuous work on the part of from one to three people, per twenty samples, for the preparational and measurement procedures. With all polymer preparation, technique of application, storage times and temperature, and even motions in coating the samples, as nearly identical as possible, the results are dependent primarily and overwhelmingly on the effects of the metal surface treatment. The intent under this contract was to make an exploratory investigation of various effects which could contribute to the overall goal, rather than to investigate one method exhaustively. Therefore, variations of treatment were intercombined as shown in the table below. For the purposes of this report, a number of types of surface treatment which yielded inconclusive results have been omitted from the data presented.

3. Adhesion of Aluminum vs. Adhesion of Copper.

In a series of ground-buffed samples, used as adherends with specially prepared polystyrene (see Sec. V A) as adhesive, it was found that copper gave a higher breaking strength than did aluminum. This agreed with the results previously reported for polymethylmethacrylate adhesive in ref. 36.

Table II.

Influence of Metal Surface Preparational Treatment

Adhesion System	Metal Treatment*	Time of Polymerization (min.)	Average Breaking Strength	
Copper-MMA	Both ground	85	330±63	(2)
	One ground, one buffed	85	128±44	(5)
	Both ground	95	1100 (one sample)	(1)
	Both buffed	95	222±67	(2)
Al-MMA	Both ground	85	424±50	(2)
	One buffed, one ground	85	36±17	(5)
	Both ground	95	1135±180	(2)
	Both buffed	95	332±24	(2)
	Both Franklin modified	95	1760±360	(2)
Copper-Polystyrene	Both ground	21 hours	1335±15	(2)
	One ground, one buffed	21 hours	751±161	(6)
Al-MMA	Both ground	30 sec. inversion time	115±29	(5)
	One ground, one polished		49±27	(3)
	Both polished under water	all cases	25 lb.	(6)
Copper-MMA	Both ground under water	127 sec. inversion time	133±43	(6)
	Both ground under water (and aged in oxygen)	"	242±39	(2)

*All grinding is grinding under distilled water.

Table III.

Adhesion of Aluminum vs. Adhesion of Copper

Prepolymerization Time	Surface Treatment	Average Breaking Strength Aluminum	Average Breaking Strength Copper
17.5 hours	Both ground	576±74	1136±131
21	Both ground	565	1335±15
21	One ground, one buffed	482±119	751±161
Unknown	Both ground	1055±115	1771±316

D. Discussion.

1. Choice of Surface Treatments.

From the results of the various types of surface treatment, there was chosen as a standard procedure for almost all subsequent samples, the treatment consisting of one member being hand ground under toluene, and the other being hand ground under water with or without subsequent oxygen aging.

2. Influence of Metal Surface Treatments.

Chemical treatment of the surface with sulfuric acid and sodium dichromate increases the breaking strength greatly as compared to grinding under water. The increase is so great that it suggests a primary chemical bond formed by a chemical reactive group from the treatment. As in earlier work, the strength of ground surfaces was considerably greater than that of polished surfaces. Rarely were samples with both surfaces polished obtained with breaking strengths of more than 5 psi, and even the polishing of only one surface of the two, while grinding the other, usually decreased the strength to less than half the strength of the ground samples. This has been explained in the literature as being due to the greater roughness of the ground surface, but there is little question that more is involved than this simple explanation. If the surfaces are examined microscopically or electron microscopically, the asperities are themselves smooth, and therefore the only question which could be involved on the roughness point of view is the increased area of rough surfaces. However, the ratio of area of rough vs. polished surfaces appears to be of the order of 2-5, whereas breaking strength ratios are of the order of more than 20 even in the less drastic changes observed in going from ground metal-ground metal to ground metal-polished metal specimens. The chemical and particularly the electrical nature of an amorphous layer, however is quite different from that of the abraded, ground surface.

Just as in the case of the toluene vs. water ground specimens, it may be noticed that the samples in which one or both surfaces were buffed were weaker than those in which both were ground, and that the mixed samples (one buffed, one ground) were weaker than either.

Surface aging in oxygen for several hours after the water grinding, and before application of the polymer, produces a higher breaking strength than that of the samples ground under water and kept under nitrogen. Up to a point depending upon the treatment, the greater the exposure to oxygen and therefore presumably the greater the thickness of the oxygen layer, the higher will be the breaking strength. However, this must be considered in light of the high strength of the toluene ground samples from which oxygen was excluded.

Among methods of sample preparation not described in the table, there were prepared several by water grinding, and immed-

ately after vacuum drying, covering the surface of one specimen with monomer and allowing it to stay there for one minute, then joining it to the other surface covered with partially polymerized polymer. The bond strengths were 133 and 252 compared with 91 and 99 for the two controls which did not receive the monomer treatment. When this was done, the authors were not aware of the somewhat similar work done by Patrick and Vaughn (32-3); the results were quite similar to those they found.

3. Breaking Strength of Mixed Samples, and Type of Break.

The fact that the breaking strengths of the mixed samples (Sec. C,1) do not lie between those of the toluene, or the water, ground samples is a striking result. Similarly, the break of an adhesion sample consisting of the polymer between two metal surfaces originally ground under water is either a cohesive break or a succession of strippages from alternate metal surfaces; that of a toluene ground sample was entirely a stripping from the surface of one metal, whereas in the mixed samples, the polymer stripped preferentially from the surface ground under toluene. Since the strengths of the samples ground under toluene were greater than of those ground under water, the explanation of the stripping of polymer is not that the use of toluene decreased the adhesion over that of the water-ground specimens. Moreover, in the mixed samples, stripping from the toluene ground surface shows that the adhesion at that face is smaller, and at a low breaking strength would appear at first sight not to agree with the fact that in the other two sets of samples, the toluene ground sample was the stronger of the two.

In general, theories of adhesion would predict that the breaking strength of the mixed samples should lie between those of the other two types, or nearly at the lower breaking strength of the two types. Since the charge equilibrium occurring in the electron atmosphere between solid adherends is an example of equilibria with long range rather than short-range forces, it is possible that the one surface in reaching equilibrium will have an effect on the second surface, through the adhesive. This will not produce an effect on the measured adhesion if polymer contacts metal directly at the interfaces; however, if there is an adsorbed layer on the two metal surfaces, between them and the polymer, different charge densities will be obtained at the interface depending upon the nature of the surface at the other interface. The proof is complex, arduous, and more voluminous than Appendix I and will be omitted. Looked at in the more usual terminology, an adsorbed layer on the metal surface will change the barrier by an amount equal to its dipole sheet potential jump. When the two surfaces each have an adsorbed layer, the charge equilibrium changes the potential jump in each adsorbed layer, and therefore changes the charge transfer at the boundary between polymer and adsorbed layer; if the break occurs between the adsorbed layer and the polymer, or within the polymer as is more likely, different values of breaking strength will be observed.

Section V

Monomer Preparation, and Chemical Effects of Degree of Monomer PurityA. Monomer Preparation.

In order that the monomers be of high enough purity so that electrical effects from small concentrations of impurities can be avoided and reproducibility of the polymer can be attained as nearly as possible, the polymers used in the experiments were prepared in the laboratory.

1. Styrene Preparation.

Styrene of over 99.5% purity by freezing point determination was prepared in the following manner. Styrene was subdivided into volumes suitable for each distillation and stored under nitrogen and refrigeration to minimize polymerization and oxidation products. The inhibitor (p-tert-butyl catechol) can be largely removed by two methods. The first is by successive treatment with drierite (CaSO_4 dried at approximately 400°C) which also removes most of the water (4). A more effective way of removing the inhibitor is with a $\text{NaOH} - \text{NaCl}$ solution (a method used by Boundy and Boyer to remove the inhibitor from distilled monomer for analysis) and washing successively with redistilled H_2O . The water is removed by successive treatment with K_2CO_3 . The monomer is distilled at 35 mm. Hg. with a reflux ratio 3:1, permitting good fractionation and providing enough material without excessive polymerization. The monomer is transferred to vials, which are sealed, inside a controlled dry N_2 atmosphere glovebag, the monomer having no chance to contact air. All the glassware used is thoroughly cleaned with $\text{H}_2\text{SO}_4 - \text{Na}_2\text{Cr}_2\text{O}_7$ cleaning solution, ammonia to neutralize it, distilled and redistilled water.

2. Methylmethacrylate Preparation.

The methylmethacrylate monomer was prepared by the same method, with the hydroquinone inhibitor being removed by $\text{NaOH} - \text{NaCl}$, three to four times, followed by water removal with K_2CO_3 , three times and a protracted fourth. After removal of the inhibitor, it was of course necessary to refrigerate the monomer, and use it as soon as possible. Only quantities sufficient for a given set of samples were prepared, and this was done just prior to the distillation. Fractional distillation was used, at $22 - 24^\circ\text{C}$, starting with a maximum of 700 ml. of dried monomer, which was totally refluxed until equilibrium was obtained in the column. Cooling of the column was with dry ice and ethyl alcohol to avoid methyl alcohol or acetone vapors.

B. Effects of Purity of Monomer on Metal Ion Migration.

In several series of copper polymethylmethacrylate samples, the copper migrated into the polymer to give a greenish color; a spot test was used to confirm the presence of copper. The sole difference between the polymer where this happened and those where it did not was the more precise purification of the monomer in the case where the migration occurred. All the inhibitor had been removed, and water had been removed to a fraction of less than 0.01% as determined by Karl Fischer Reagent (27). If the water content was permitted to rise to 0.10% or above, or other impurities to be present, the migration did not occur.

Apparently this indicates that copper migrates into areas otherwise occupied by water. When the electrons diffuse from polymer to metal, the electrical field set up encourages the migration of the metal into the polymer; another explanation which may account for the behavior is that the presence of the water (of high dielectric constant) reduced the local electrical fields below those necessary for copper migration.

The green color appears on areas which have apparently cleaved from the nonoxidized metal surface, and therefore are also undoubtedly in the small thickness of polymer which has been shown to remain on the metal surface (p. 77), so that the copper must migrate from the oxide free top surface. Such metallic migration has been observed in the literature with polyacrylic acids, but to our knowledge, it has not been observed with polymethylmethacrylate.

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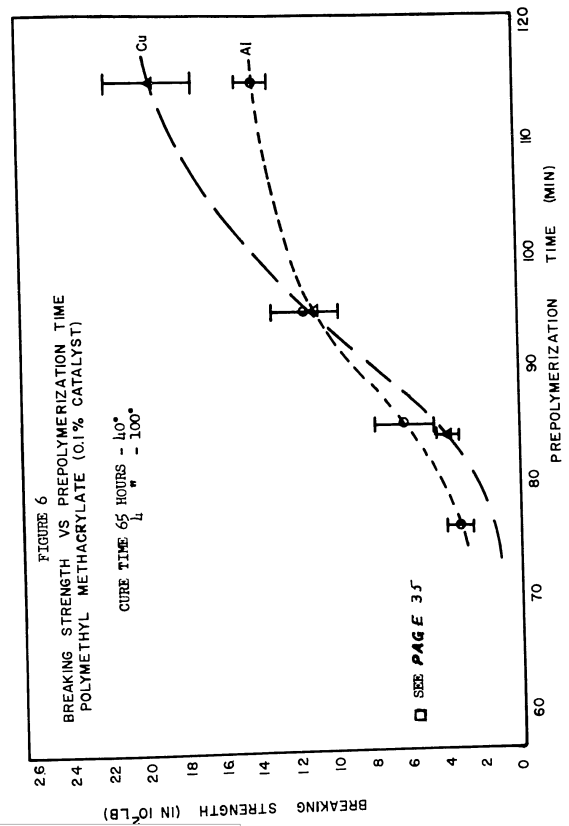
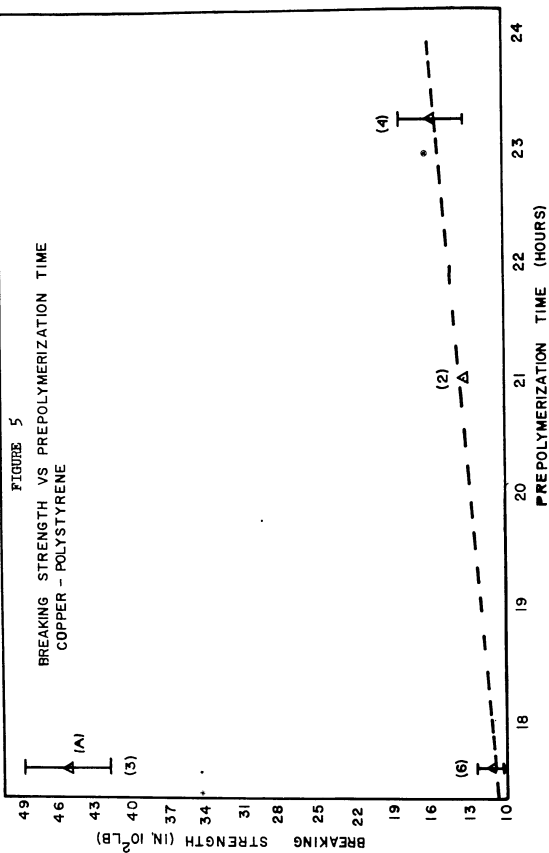
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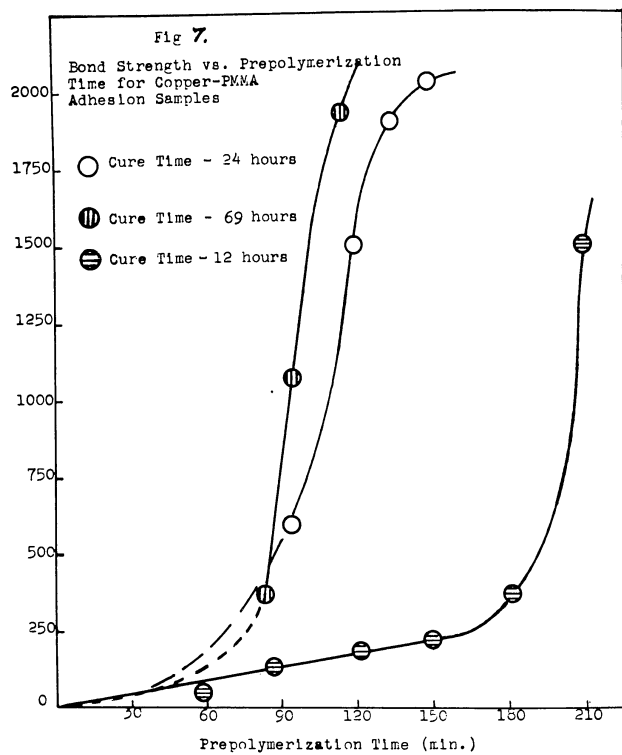
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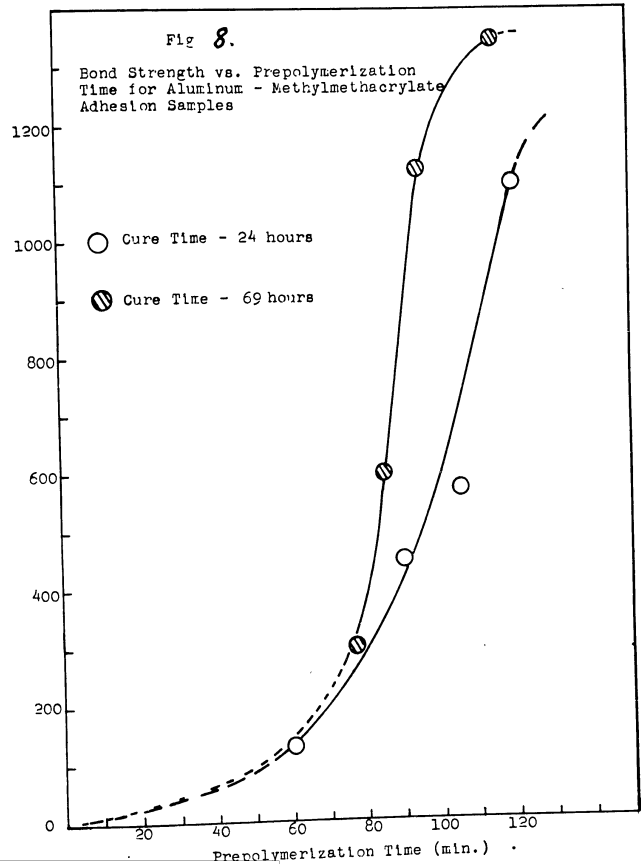
Apparently this indicates that copper migrates into areas otherwise occupied by water. When the electrons diffuse from polymer to metal, the electrical field set up encourages the migration of the metal into the polymer; another explanation which may account for the behavior is that the presence of the water (of high dielectric constant) reduced the local electrical fields below those necessary for copper migration.

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SEC. VI

EFFECTS OF PREPOLYMERIZATION CONDITIONS ON BREAKING STRENGTH

A. Experimental.

In earlier work, it had been found that the breaking strength of the specimens prepared with polymethylmethacrylate adhesive depended upon the time of prepolymerization, i. e. the time in which polymerization was carried on in the absence of metal, as contrasted to the time in which cure of the adhesive was performed after application to the prepared metal surfaces. In the present work, this was extended to cover additional ranges with polymethylmethacrylate, to polystyrene, and to copper, aluminum, and nickel specimens.

Prepolymerization was performed in sealed glass vials, filled in a dry nitrogen atmosphere inside a glove bag. If catalyst was used, this was added to the monomer distillate inside the glove bag after sufficient time in the nitrogen atmosphere for it to lose any excess moisture; catalyst was only used with polymethylmethacrylate. After the vials were filled, they were stoppered with aluminum foil surrounding corks also aged in the nitrogen atmosphere; the aluminum foil was precleaned with organic solvents, and repeatedly washed with distilled and redistilled water, and vacuum dried. The glass vials were obtained from the Kimble Glass Company all from one special batch with precautions to ensure that they were subject to identical treatment during manufacture, and were cleaned identically, partially constricted below the mouth, and maintained in the nitrogen atmosphere for aging for at least several hours before adding the monomer distillate. Immediately after filling and stoppering the vials, they were brought out into the air, and the necks were sealed off under the stopper with a flame, and then the vials were refrigerated overnight.

The next day prepolymerization was performed. The vials were placed in a tray of water (for temperature uniformity), in a precision oven (tested by thermocouple beforehand and found to maintain uniform temperature to 0.1°C over the volume of the oven, and to 0.5°C over the time of prepolymerization) at 70°C . Here they were polymerized to the desired viscosity as determined by inversion time (see below) or to the desired number of hours.

B. Effect of Prepolymerization Time.

In the cases of both aluminum and copper, the breaking strength of the adhesive bond increases with the time of polymerizing the monomer before it is joined to the metal surfaces. With metal samples of 1.125 inch diameter, the increase in breaking strength with increased prepolymerization time is shown in Figs. 5, 6, 7 and 8.

1. Styrene.

Styrene (Fig. 5) shows a nearly linear increase of breaking strength with prepolymerization time. The average values with their r.m.s. deviations and the number of samples represented are shown. The value (a) is from the same series as the samples below it, the values falling in a distinct range of values due to the properties of the polymer as will be discussed in detail below for polymethylmethacrylate. The linear relationship is for the less viscous of the two phases.

2. Methylmethacrylate.

Figure 6 shows the increase of breaking strengths with prepolymerization time of samples ground under water (see Sec. IVC) both for copper and for aluminum samples. In Figs. 7 and 8, these are replotted and compared with the results obtained at different total cure times in WADC Technical Report 56-158; the present data are the curves at a total cure time of 69 hours performed with additional precautions as described in the text, and with monomer taken off in only the desired portion of the fractional distillation.

The crossing over of the curves for copper and for aluminum in Fig. 6 is of especial interest. Evidently at low prepolymerization times, the presence of the copper adherends depresses the final strength obtained by cure of 65 hours at 40°C and 4 hours at 100°C more than does the presence of the aluminum adherends, but at higher prepolymerization times, the reverse is true. (The single square on the right of the diagram refers to material prepolymerized for 60 minutes, and then cured for 152 days at room temperature, and shows the advantage of low temperature curing, if the time is available for it.)

3. Relation of Prepolymerization Strengthening to Total Cure Time

In Fig. 7, the effect of prepolymerization time is seen to be greater at the higher total cures. At 12 hours total cure, prepolymerization of less than 3 hours produces little increase of strength. At 24 and 69 hours respectively, the effect of prepolymerization shows up strongly at 100 and 80 minutes respectively. This is with copper adherends. In Fig. 8, the similar effect is shown for aluminum adherends, and the same type of increase of total breaking strength produced by prepolymerization is shown; again the effect of the prepolymerization is greater for higher cure time.

With the exercise of some imagination, it can be hypothesized from the figures that there is a definite ultimate breaking strength obtainable from prepolymerization (as prepolymerization time increases), and that this strength will increase with total cure time; however, confirmation of such a hypothesis goes beyond the present data. It is noticeable, however, that the amount of prepolymerization time necessary before the effect becomes significant (i. e. rapid rise of the curve) changes rapidly during the stages when the amount of total cure is small, and slows up after the cure time has reached values which yield quite viscous material or nearly crystalline material. It should also be recognized that carrying either cure or prepolymerization too far results in unsuitable material.

C. Effect of Inversion Flow Time on Breaking Strength.

1. Definition.

The inversion flow time is defined here as the time for a given amount of liquid (5 ml.) to flow down a glass vial (3.5 inches long), while the meniscus is observed, and a reproducibly slow rate of rise of the bulk meniscus is taken as the stopping point. This control method was instituted because of the desired high viscosity material and produces a suitable parameter, in which the variation in time is so small as to produce considerably less error in final results than do other factors. It has the desirable property that it permits determining the state of the material, and at the same time using the measured material, which would not be possible if traditional viscosity measurement methods were used because of time under foreign

atmosphere and contact with additional surfaces.

The inversion time may be taken as a linear function of the viscosity of the material, and being a melt viscosity of polymer in low molecular weight polymer, is roughly related to the molecular weight by the relation,

$$\ln n = A + B M_w^n$$

where M_w is the weight average molecular weight, where n is probably nearly $1/2$. The relationship actually is more complex than this, since for the range desired for the breaking strength experiments it was necessary to go to much more viscous polymer than is usually used in experiments, and two or more mixed phases were present in the material. This type of uncertainty with the more viscous material is characteristic of work in this field, and is responsible for limiting ordinarily reported results to lower ranges than those studied here.

The existence of at least two phases was observable visually. The first phase flows very rapidly, while at the same time the more viscous phase has started to flow. A third phase appears to be present, which is too viscous to be effective in modifying the inversion time, since its additional flow is slow enough to be excluded from consideration with the stopping point set in the experiments. Whether additional phases were present could not be determined visually.*

The viscosity measured by the inversion flow time is essentially a melt viscosity, and is determined primarily by the viscosity of the second phase.

2. Metal Surface Preparation.

In the inversion flow time measurements, all samples, whether aluminum, copper, or nickel, were prepared by the technique chosen as a result of the study of metal surface preparation techniques. The top member of the adhesive bond was prepared by grinding with the special 600 mesh alumina under toluene, and the bottom member was prepared by grinding under distilled water. In all cases, the break was essentially an adhesive stripping from the top member, so that what is being measured is the adhesion at or near the interface, rather than the cohesive strength of the adhesive.

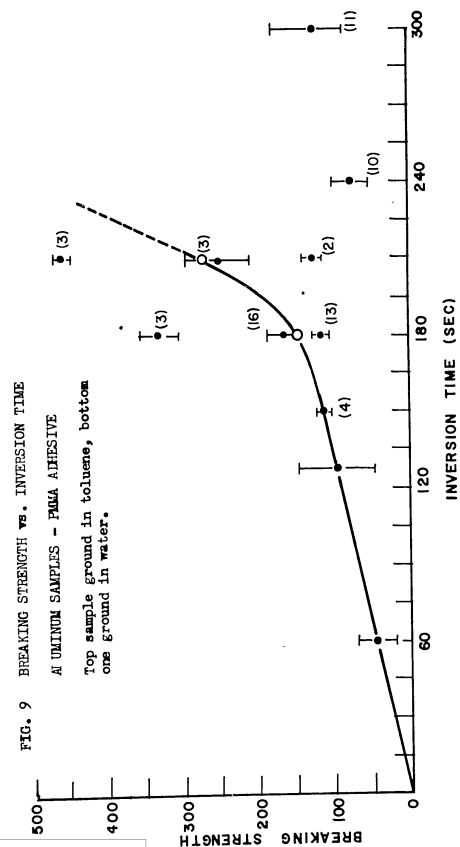
3. Breaking Strength per Unit Area.

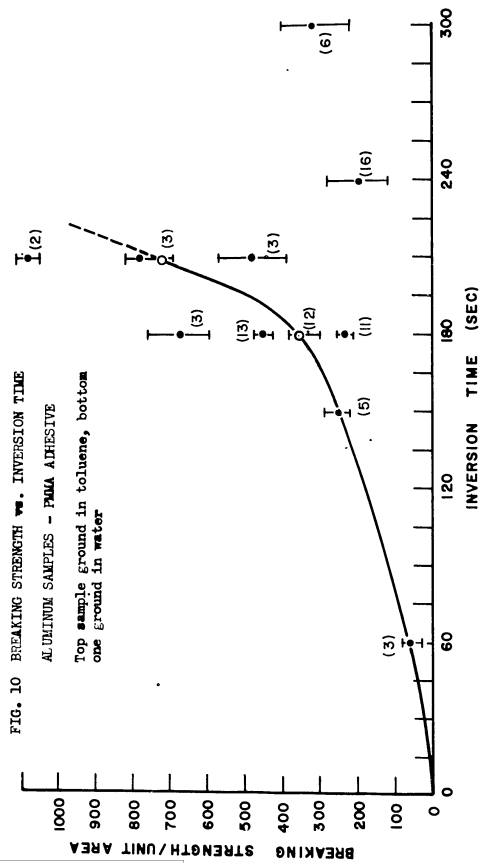
Because of the spread of values at the higher viscosities (this type

* Although this was not definitely confirmed, we have reason to believe that the three phases were, in order of decreasing viscosity,

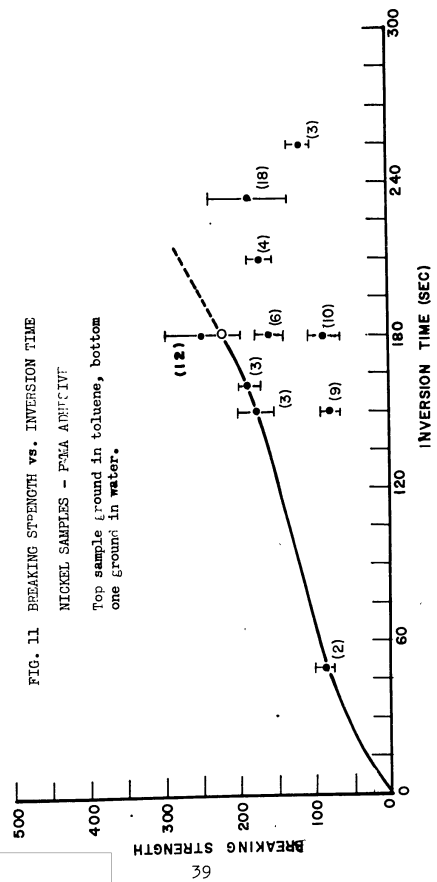
- a cross-linked, slightly swollen, essentially insoluble polymer
- a monomer swollen high polymer
- monomer with a trace of high polymer dissolved in it.

Differences in the relative proportion of the three components, will of course affect the observed breaking strength.





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of wide variation is commonplace in experiments at such high viscosities), a study was also made of the breaking strength per unit area, as related to the inversion time, in one case, namely that of aluminum adherends. Because of the time-demanding requirements and arduous nature of the work required in the accumulation of this data, and since, although it reduced the rms error, it did not make appreciable difference in the general behavior of the curve, it was not extended to other adherends.

The metal areas which had been bonded and stripped adhesively were examined microscopically, and by photographic enlargement. Distinction was possible between areas (including micro-areas) which had not originally been bonded, and those which had been bonded and from which adhesive had been stripped. The latter areas were determined by superimposition on small square graph paper, and counting of individual squares, with the original $\frac{1}{4}$ -inch diameter specimen face enlarged to three times diameter, i. e. $9 \times$ area.

4. Aluminum Adherends - Polymethylmethacrylate Adhesive.

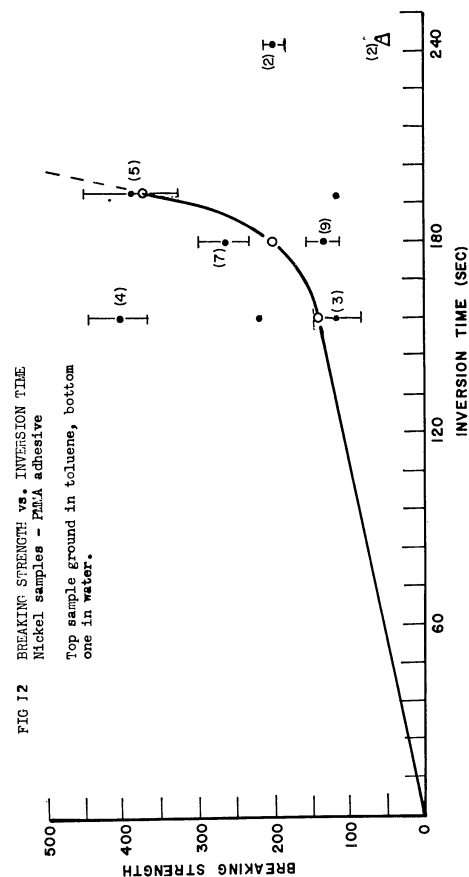
The curves in Fig. 9 of the total breaking strength vs. inversion time, and Fig. 10 of the breaking strength per unit area vs. inversion time are similar. The values fall into distinct ranges after the viscosity has reached a high enough value. Starting at 180 second inversion time, three distinct ranges are seen. At 240 seconds inversion times, the most viscous phases are now too far polymerized to flow easily, and the ranges show the effects of the more fluid phase. Material from the fluid phase is now acquiring more of the characteristics of the second phase, and the molecular weight and therefore the breaking strength increase less rapidly than if the more viscous phases were being considered, i. e. similarly to the initial portion of the curve rather than to that after it turns up towards a steeper rise.

In Fig. 10, the values of breaking strength at 180 seconds inversion time altogether cover a set of five batches prepared at different times over a more than three month interval, from different bottles of monomer. The same painstaking procedure was taken with each batch, except that though Q and R had been prepared by the technique described in the text, considerably more effort and safeguards were used with V, W, and X. The impurities were brought to a lower content, water content to less than 0.04%, and the distillation fraction of monomer used was between a fourth and a third, only, of the original purified monomer. In each of the ranges from the top down, there are samples from the following batches: first - batch X only; second - batches Q, R, X, V; third - batches X, V; fourth - batches W, V. In view of these results, the data at inversion times of 210 seconds and 240 seconds were taken from a single batch each.

5. Copper Adherends - Polymethylmethacrylate Adhesive.

The variation of breaking strength with inversion time for PMMA - Copper is shown in Fig. 11. At least two, and possibly three breaking strength ranges are observed. Again, the samples used were: top adherend, toluene ground, bottom adherend water ground, and adhesive separation was obtained. As before, the open dots are the mean of the several ranges. Above 180 seconds inversion time, the breaking strength of the samples composed primarily of the more viscous material presumably increased rapidly, and fall off the graph;

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physically this means that the more viscous material was sufficiently rigid after 180 minutes prepolymerization, so that it failed to participate in the bonding during cure, or could not yield sufficiently to applied stress to exhibit its full strength.

6. Nickel Adherends - Polymethylmethacrylate Adhesive.

Fig. 11 shows the variation of breaking strength with inversion time for PMMA - Nickel. This curve is also similar to Fig. 9, the breaking strength being displaced to a slightly higher value than for copper. Three ranges are again apparent from the data at 150 minute inversion time, and from breaking strength per unit area data; insufficient data is available with respect to the latter to present a separate curve.

7. Discussion.

The lower end of the curves of breaking strength vs. inversion time should approach zero breaking strength. Within the ranges investigated, there appeared to be no dependence of breaking strength on adhesive thickness; this is in agreement with the theory in WADC Technical Report 56-158. However, from the technical point of view, at lower inversion times, the viscosity would be small enough so that problems of maintaining suitable adhesive layer thickness in the sample during cure would multiply. Both evaporation, and flow out of the sample, during cure in the oven would be accentuated by the presence of very large quantities of monomer or very slightly polymerized material. Whether the breaking strength would actually approach zero or a value near to zero as the viscosity became very small is academic from the point of view of adhesion technique, and from the point of view of this problem which is devoted to a solid state concept.

8. Breaking Strength vs. Amount of Initiator.

In the table below, there are presented relative breaking strengths for samples of copper and aluminum adhered with polymethylmethacrylate by the techniques described in the text, in terms of whether the amount of benzoyl peroxide used in catalyzing the polymethylmethacrylate was 0.05% or 0.1%.

Table IV.

Effect of Initiator on Breaking Strength. 1.125" Diameter Samples.				
Prepolymerization Time	Polymerization Time	Breaking Strength (psi)		% Initiator
		0.05%	0.10%	0.20%
Copper - PMMA		Total number of samples measured		
142	60	512 ± 161 (4)	1019 ± 292 (7)	1072 ± 240 (3)
120	60			
87	60			
142	210	343 ± 26 (5)		
120	210		880 ± 412 (7)	
142	360	481 ± 134 (4)		
120	360		695 ± 224 (5)	
Aluminum - PMMA				
142	60	651 ± 252 (5)	1470 ± 220 (4)	1629 ± 242 (4)
120	60			
87	60			
142	210	492 ± 157 (2)		
120	210		1626 ± 370 (4)	
142	360	388 ± 124 (4)		
120	360		1734 ± 44 (3)	

In order to obtain comparable results, it is necessary with the greater amount of benzoyl peroxide to cut down somewhat the prepolymerization time. In all cases, however, the effect of more initiator is to make a stronger adhesive bond. If this were carried out beyond the limits of this study, there could be obtained a product which was weaker and even useless for adhesion purposes. However, within this practically useful range, the result is a clear increase in strength. This is probably due to faster polymerization primarily, and therefore a more effective formation of a suitable adhesion layer, without loss of bonding area or material. It is obvious that there will be some effect on the electrical properties of the bond from a) the presence of more initiator residue, b) the lower molecular weight distribution with faster polymerization, c) the different cross-linking and chain configuration.

It is noticeable that the variation between samples under similar conditions is higher for aluminum than for copper. However the data in Table III, is from earlier work under this contract before all the minutiae of technique which were later used, had been developed.

D. Inhibition of Polymerization by Metals.

The fact that metals inhibit polymerization is stated in the literature,

and is supported by the beneficial effects upon breaking strength which are produced by prepolymerization as just described. However, certain of the electrical work performed in connection with this project, interpreted by existing theories in organic chemistry, indicated that the transfer of charge between metal and monomer in particular cases would be such as to favor polymerization. As a confirmation of the inhibiting effect on methylmethacrylate, a number of powders of aluminum, copper, and zinc, were mixed with purified monomer, and placed in vials under the procedure described above, and the length of time which was necessary for the material to become quite viscous during cure at 70°C observed, and compared with that when no metal was present. Frequent shaking of the samples enabled a maximum contact of material with the metal. Viscosity was determined by inversion flow time. The cure time for a given viscosity of material to form was increased from between $3\frac{1}{2}$ and 5 hours, depending on the viscosity chosen, to times up to well over 24 hours. After two days of cure, the polymer became completely solid.

The same effect was observed when a thin layer of monomer over a surface of the metal powder was heated at 70°C.

This confirms that for the purified monomer which we used, metals did have an inhibiting effect, and therefore supports the view proposed for the beneficial effects of prepolymerization. It also shows, however, that the inhibition is merely a slowing down, and not a preventative of polymerization. The same view is supported by the experiment on application of monomer to the surface of one adherend by dipping, before joining it to the partially polymerized material already applied to the other described in Sec. IV, D, in which the breaking strength was increased from an average of 95 psi for non-dipped adherend, to 192 psi for the dipped adherend.

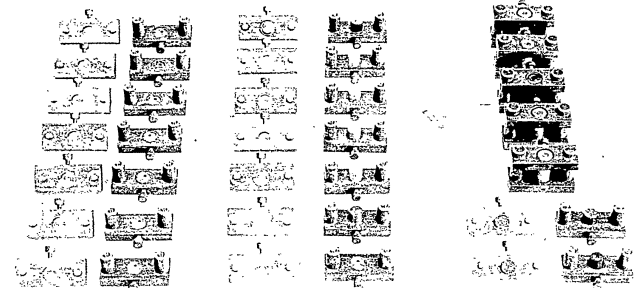
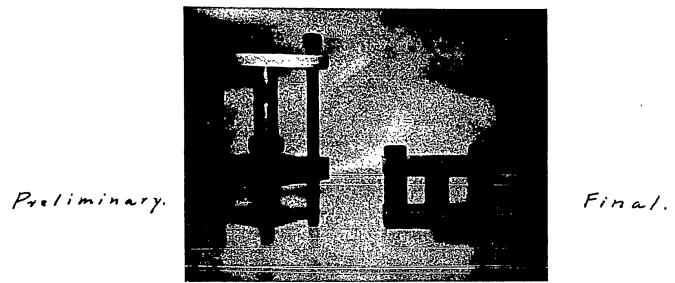


Fig. 13. Sample holders for assembling adhesion specimens.
Top: The preliminary and final design of the holders.
Bottom: Set of holders showing shim stock.

SECTION VII

THE EFFECTS OF CURING (POLYMERIZATION) TIME AND CONDITIONS ON BREAKING STRENGTH

A. EXPERIMENTAL.

1. Special Holders for Sample Preparation.

The steel collars used to hold the sample in place during cure in the work previously reported were found to give insufficiently good control of the adhesive layer thickness. Accordingly, special holders were made up for this purpose. The first such set made up consisted of rigidly mounted brass columns in an aluminum block, with a crosspiece joining them; the crosspiece could be removed or attached by separate screws. Both in the block and in the crosspiece, there were accurately centered threaded rods which screwed into the specimen, and relative height adjustment could then be done by means of a nut-and-threaded rod section on the bottom support which passed through the aluminum block. While this improved the control of thickness and registry of the two halves, it was found to depend upon the degree of correspondence of the bore of the threaded hole in the half specimen with that of the thread on the support. Accordingly, an improved holder was designed.

This holder, which was used thereafter for all the 1/2-inch diameter specimens is illustrated in Fig. 3. It is sufficiently accurate so that matched tops and bottoms must be used together. The holes in the top and bottom portions are bored accurately perpendicular to the plane of the horizontal surface, and have in them a concentric split collar of uniform thickness. The specimens are placed inside the latter, and after the suitable vertical position is attained, are held tightly in place by tightening the thumb screw. The exact registry of the two halves is assured by the perpendicularity of the bore to the surface, and by the fact that the bottom surface of the top cross member is maintained in a plane perpendicular to the axis of the bore by being placed on an accurately machined flat surface of the two vertical rods at the ends, and held in place by the threaded nut with planar bottom head surface. Each specimen is placed in the holder, thickness of adhesive layer is determined by the use of a shim (cleaned with ethyl alcohol and maintained in a vacuum dessicator and under nitrogen till used), and then the halves of the holder are separated by removing the top portion by means of the two screws at the ends.

2. Preparation of Sample.

In making up the samples, the bottom member is placed in the holder, the top member is taken from its dessicator, set in place in the holder with the clean shim stock between it and the bottom member, and the split collar is tightened around the top specimen. The top member and its holder are removed together, polymer poured on the bottom member and the top member put on. In this operation, 1) the polymer must have the desired viscosity within fifteen minutes of the finish of the time of grinding, or regrinding must be done, so that the finished surface (even though maintained under a nitrogen atmosphere) does not wait too long; 2) the dessicators are maintained under vacuum with not more than three or four samples and these are opened successively as needed just prior to adjustment of samples in

holder; 3) the samples must be lined up by one experimenter for the application of the polymer just by the time that the experimenter who is applying it is ready; 4) the latter must have the vial freshly broken and tilted to the point at which the polymer has flowed down to and is ready to leave the bottom of the vial when the samples reach him; 5) he must apply it in not more than two motions per sample, as the samples pass him, and achieve a complete coverage without bubbles (if bubbles appear the material is too viscous or improper technique is evident); 6) he must apply the polymer without touching the bottom surface with the vial, but with a minimum of distance for the polymer to flow between vial and metal. If these conditions are not achieved, particularly numbers 4, 5, and 6, the batch is rejected, and another batch of polymer is prepared, samples cleaned again and reground, etc. As soon as the polymer is poured onto the set of three or four samples, another experimenter places the top sample on, and fastens down the crosspiece. When twenty are poured, they are immediately placed in the oven. By this procedure, the top metal member, if prepared for minimal oxidation, is exposed to the air for not more than 15 seconds. As a check on whether even this time would affect the measured breaking strengths, in the case of aluminum (which being more active was expected to be more sensitive to exposure), several batches were made by the same technique with aluminum adherends completely inside the dried nitrogen atmosphere in the glove bag, and the breaking strengths compared with those when performed in air. There was no apparent difference in breaking strength between the two procedures from any thin oxide layer which could have been developed during the air exposure.

3. Polymerization Schedules.

Unless otherwise specified, the polymerization schedules followed were:

PMMA	0.10% benzoyl peroxide	40° C	44 hours
		100° C	4 "
0.05% " "		40° C	72 "
		70° C	18 "
		100° C	4 "
Polystyrene	no catalyst	90° C	8 "
		refrigeration	12 "
		90° C	7 days 4 hrs.
		120° C	2 days
		140° C	2 days

The refrigeration was introduced to control the rate of polymerization, retarding it in the induction period of polymerization. The length of refrigeration time was chosen largely for convenience and is probably not critical. These schedules resulted from both previous work performed by us and described in part in WADC Technical Report 56-158, and from a detailed study of the effect of temperature and time variation on breaking strength and on the coverage (metal to metal bonded area) of the specimens, as observed after break. Much of the latter is purely routine and provided information as to what not to do; some of it is reported here, where it is



Fig. 14. Dry nitrogen atmosphere glovebag used in handling the monomer and test runs for making the entire adhesion sample.

felt to be of interest.

B. EFFECT OF VARIATION OF SCHEDULE ON BREAKING STRENGTH.

1. Polymethylmethacrylate.

For polymethylmethacrylate, temperatures below (36°C) and above (70°C, 100°C) the optimum of 40°C were found to result in lower breaking strength. Similarly, the wetting (extensiveness of a polymer layer thick enough on the metal to be visible but not necessarily giving an all-over metal to metal bond) was lessened by the lower and higher polymerization temperatures. The exact reasons for this temperature effect are not clear, but we speculate that at higher temperatures, an increased fluidity and increased rate of polymerization are conditions unfavorable to having the polymer flow into and remain in volumes of polymer which extend from metal to metal. At the lower temperatures, it may be that a contrary tendency begins to dominate, namely that the decreased rate of polymerization permits a longer time for a material of a given viscosity to flow and decreases metal-to-metal bonding; the 36° polymerization was done in a water tight container lowered into a constant temperature bath, whereas in the 40° polymerization the vials were placed as usual in the oven. Sample effects of temperature on breaking strength follow:

40° oven	125 ± 79 (4)	40° oven	129 ± 37 (7)
36° bath	76 ± 17 (3)	36° bath	70 ± 18 (3)

Similarly, replacing the final curing temperature in the 0.10% catalyzed PMMA (100°C) by 200°C, lowered the average breaking strength from

163 ± 78 (4)	to	46 ± 28 (6)	for aluminum
181 ± 48 (13)	to	25 ± 5 (3)	for nickel.

The inversion flow times in the last set of figures were (from right to left on the upper line and then right to left on the lower line), 132 sec, 141 sec, 150 sec, 141 sec.

2. Polystyrene.

Variation of time of polymerization at a given temperature was one of two factors (the other being storage of the distilled monomer for several days in a vessel flushed with and containing nitrogen) in increasing the breaking strength of polystyrene - copper samples. Polymerization at 90°C for 10 days instead of the above schedule increased the breaking strength of the 1.124" diameter samples from 1525 ± 225 (4) lbs. (23½ hours prepolymerization) to 4000 ± 700 (6) lbs. (24 hours prepolymerization).

3. 1 Minute Inversion Time PMMA.

Increase of polymerization time both on copper and on aluminum samples increases the strength. Typical figures at 70°C are:

Aluminum		Copper	
	Avg. Strength		Avg. Strength
2 hours	30 lbs.		
6 "	42 "	6 hours	141 lbs.
18 "	25 "		
24 "	130 "	24 "	110 "
48 "	103, 157 lbs.	48 "	190 "
		(44 hrs at 70° 4 " at 100°)	218 ± 73 (4).

4. Copper Top - Aluminum Bottom Mixed Samples.

The following data for copper top - aluminum bottom mixed samples ground under water and 0.05% catalyzed PMMA show the increase in bond strength with increasing time of polymerization at longer polymerization times.

Polymerization Schedule	Breaking Strength
72 hours 40° 18 hours 70° 4 hours 100°	720 ± 269 (6)
46 hours 40° 15 hours 70° 1 hour 100°	339 ± 50 (3)

5. Aluminum Samples.

The effect of prepolymerization has been treated in another section, but the increase of breaking strength when prepolymerization is combined with a change in the polymerization conditions is illustrated for aluminum samples in the following data:

Prepolymerization	Polymerization Conditions	Average Breaking Strength
85 min. 70°C	65 hr. 46° 4 hr. 100°	729 ± 26 (3)
95 min. 70°C	65 hr. 40° 2 hr. 70° 4 hr. 100°	1135 ± 180 (3)
100 min. 70°C	132 hr. 40° 4 hr. 100°	1658 ± 382 (3)

C. UNCATALYZED METHYLMETHACRYLATE POLYMER.

Methylmethacrylate polymer was prepared without catalyst (in analogy to the successful preparation of uncatalyzed polystyrene) after an exhaustive search of the literature as to conditions in which this could successfully be accomplished. The resulting product gave a much lower bond strength than did catalyzed material of the same viscosity. The uncatalyzed material becomes unworkable at the viscosities normally used, and observable gelation appears, evidencing greater degrees of cross-linking than for the catalyzed material at the same viscosity. Probably the lower bond strength is attributable to 1) the effect of crosslinking in the polymer prior to application, 2) the lower degree of polymerization when poured, and 3) the slower rate of polymerization after pouring.

SECTION VIII

EFFECT OF SAMPLE GEOMETRY

A. Patterns of Adhesive on Broken Samples.

1. Types of Patterns.

As stated elsewhere, during the course of this investigation, it was decided to replace the 1 1/8 inch diameter surfaces with circular boundary by small samples of circular cylindrical form with a diameter of 1/2 inch. This was done in order to reduce the effect of inhomogeneities and scratches which can occur more frequently on the larger samples. An equally cogent reason was that the broken samples tended to show areas in which the adhesive exhibited fernlike patterns, the overall area involved sometimes being circularly symmetrical, at other times extending over only a small portion of the specimen. With the smaller samples, the fernlike pattern almost always extended over a region which occupied the center of the specimen, usually out to a distance of 1/4 to 1/2 the radius of the circular face. Sample photographs are shown in Figs. 15-19

2. Causes of Patterns.

The basic cause for patterns on the specimens is that methylmethacrylate shrinks during cure. At 20°C, the density of the monomer is about 0.956, and that of the fully polymerized material is about 1.186, so that at that temperature, there has been a shrinkage of some 21% during polymerization, depending upon the completeness of the polymerization. Because of this shrinkage, and because of the fact that the material polymerizes exothermically and therefore is prone to the formation of bubbles which are trapped by the viscous fluid during polymerization, the technical precautions which must be incorporated into the casting or molding of large objects are formidable. In the preparation of an adhesive bond between metals, the initial layer of monomer which is placed upon the adherend shrinks, flows, laterally, and evaporates out of the space between adherends. This is a major reason that prepolymerization confers advantages on the final bond; it results in a partially polymerized, viscous material which clings to the adherends, and yet is not volatile enough so that appreciable loss occurs from escape of vapor.

Nevertheless, shrinkage during cure can take place in a variety of ways, and since characteristic types of patterns were observed, there should be some correlation with sample geometry, cure conditions, and manner of breakage of the finished bond. Inhomogeneities of the metal surface cannot be accepted as primary cause for the structure of the patterns because of the similarity of the pattern from sample to sample.

It was therefore apparent that the causes of the patterns, in temporal order were:

- (1) Distribution of initial wetting of the metal;
- (2) Shrinkage of plastic during cure;
- (3) Plastic flow during stressing;
- (4) Mechanical or electrical phenomena taking place during break.

All of the above mechanisms should be sensitive to the geometry of the specimen, the latter three somewhat more so than the first.

It was also observed that in many specimens there was a ring of plastic outside the fernlike patterns, which extended from the rim inwards for a distance of from 1/10 to 1/2 of the radius. This ring was relatively uniform in comparison with the patterns in the interior, but closer examination would show a small amount of structure. Examples are shown in the figures.

Since this behavior appears related to the mechanical behavior which depends upon electrical charge, it was examined further.

B. Experimental.

1. Construction of Modified Samples.

Samples were constructed with modified geometry, but retaining the circular symmetry. Two types were prepared. The first was made with smaller total area by machining off a ring of metal on the circumference of a standard sample to leave a circular area of 1/4, or one of 5/32 inch diameter; the depth of cut was large enough so as to eliminate perturbation by the area (at a lower depth) which was removed at the surface, or by the curved walls of the sample. Nickel samples were used for this. The other was prepared by machining (on a lathe) away the center portion of the top member up to 1/4 or 5/16 diameter from the center, to a depth of 0.002" or 0.005". Aluminum and nickel samples were prepared in this manner.

The former (ring removed) specimens were prepared for bonding, by the usual techniques described elsewhere in this report. In the case of those from which a thin layer of center portion had been removed, a special treatment was used in order to maintain control of the depth of the space. They were refluxed in acetone and benzene to remove oil or foreign material and then ground under water and then toluene (since it was desired to have the strippage occur from the modified specimen) by the following modified schedule:

Grind two minutes with light slurry of distilled water and alumina;
Grind two minutes with light slurry of toluene and alumina;
Grind two minutes with fresh light slurry of toluene and alumina.

Otherwise the samples were handled and adhesive poured as described in the description of procedures elsewhere in this report.

2. Patterns on the Reduced Size Circular Face Specimens.

The 1/4 and 5/32 inch samples were bonded to the 1/2 inch diameter samples. Miniature patterns were obtained corresponding precisely to those obtained in bonding together 1/2 inch specimens. The relative amount of metal to metal bonding as compared to nonbonded areas is not a function of the area, within the limits investigated, although it may be a function of the shape of the area.

3. Patterns on the Outer Ring of Metal Specimens.

The hollowed metal area and corresponding area on the matching (but not machined) specimen are wetted with polymer, but the polymer does not usually extend from one to the other specimen.

The 1/4 inch nickel specimens hollowed to 0.002" depth yielded the best results. With these specimens, shrinkage during cure, or other effect was not great enough to prevent all metal to metal bonding in the hollowed area, but in a large number of cases, the areas were definitely confined (and defined). With improvement in technique, it was also possible to obtain similar results on the aluminum to a large degree, though this was more difficult to do. The type of patterns obtained are shown in Figs. 17. To a large degree the patterns on the standard samples could be reproduced on these special samples.

Two general types of patterns were obtained. The first, Figs. 16, consisted of a thin snakelike ridge connecting the two halves of the sample, with tributaries coming into the main pattern at relatively greatly separated intervals, and with the majority of the surface covered with a closely adhering layer of polymer which did not extend the whole way from sample to sample, and therefore contributed nothing to the adhesive strength. The second type was the fernlike pattern mentioned above; in the spaces between the fronds of the ferns, there is apparently also a closely adhering layer which is bonded to only one of the two metal surfaces. Before break, in either case, the polymer distribution must give the impression of a somewhat corrugated polymer coating on either member of the adhesive sample, the corrugations in some cases extending up to the point where they meet; these regions of meeting constitute the adhered regions and are alone responsible for the adhesive strength of the sample.

The fernlike patterns occurred only at the higher degrees

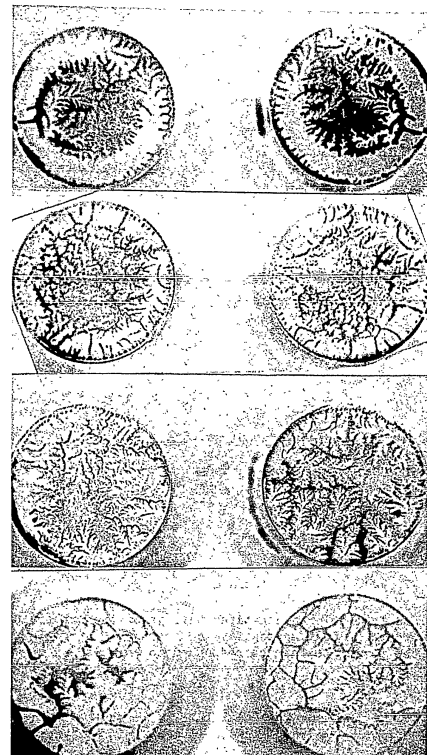
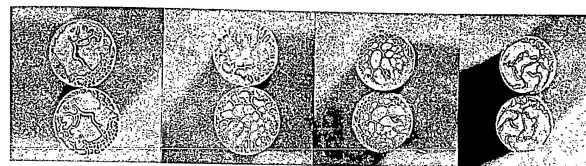




Fig. 15 1.125" metal samples with polystyrene. The distinct fern-like pattern is observed, being more pronounced on the copper samples. One metal member was ground under water, the other buffed with emery paper. Break was within the polystyrene layer. The samples, in order, and breaking strengths are:

186	Copper	560 lb.
185	Copper	582
188	Copper	977
219	Aluminum	381
240	Aluminum	345

Shown are prints from colored negatives which show the pattern of sprayed fluorescent powders indicating positive or negative charge. Upon examination, the powder pattern corresponded to the pattern the polymer formed.



Aluminum - PMMA samples with line structure (snakelike or cellular) where the bonding polymer is entirely stripped (except under high magnification) from the member ground under toluene.

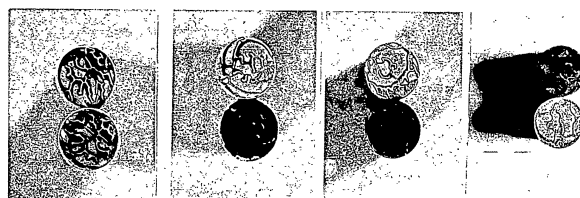


Fig. 16

One nickel and three copper samples (respectively) with PMMA. Snakelike structure strips predominantly from the toluene ground surface (the dark surface of copper).

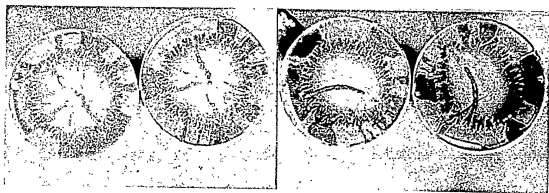


Fig. 17

Nickel samples showing reproducibility of ring.

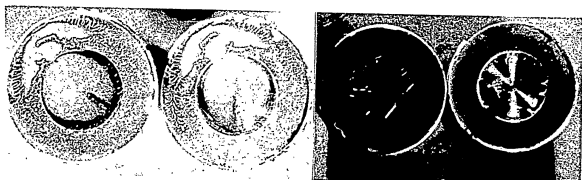


Fig. 18

Nickel samples with top member made as a ring to confine the metal area. Confining was fairly good.

Fig. 19

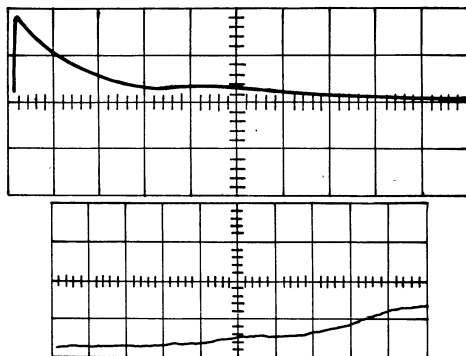
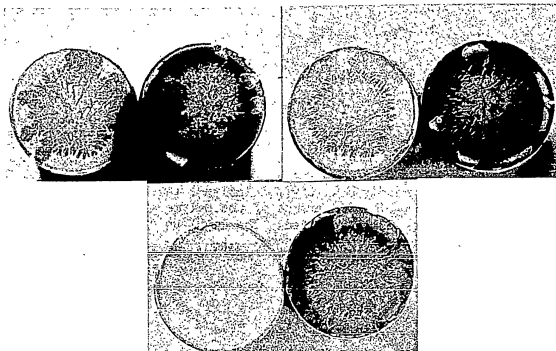
Copper samples showing reproducibility of ringed polymer area. Areas of apparent stripping from the metal show very thin polymer layers only under high magnification. The fern-like appearance of the polymer is probably primarily caused by shrinkage upon polymerization. The light colored member is oxidized while the dark one is ground under toluene.

Fig. 20

PMMA - 1% acrylic acid copolymer between buffed and a ground (in H_2O) copper surfaces. The same sign of charge on the polymer is observed as with PMMA and the curves are similar.

X-013 Aluminum - PMMA

Showing the initial portion of the rising portion of a curve.



of polymerization as indicated by larger values of the inversion time of the adhesive (Sec. VI C). At smaller inversion times, the snakelike pattern was found. However, at the higher inversion times, snakelike patterns were also found sometimes. The characteristic inversion time above which the fernlike pattern would be found differed for the different metals. Including specimens which were not specially prepared for this study, but were prepared by the usual finally adopted technique, it appears that the inversion time necessary before the fernlike patterns are found, are, for nickel specimens 60 seconds, for copper, 60 or 120 seconds, and for aluminum, 180 seconds.

4. Correlation with Breaking Strengths.

With specimens of the same metal demonstrating the same type of pattern, the breaking strengths normally lie very closely together, i.e. within a few pounds out of 3 - 400 lbs. However, occasionally such a specimen will show a considerable divergence from the breaking strengths exhibited by almost all the specimens of this type. The result is not a random distribution of breaking strengths, but an overwhelmingly large group closely together, with a very few showing very different strengths; the difference in such a case is always that the specimen which deviates from the remainder is much weaker.

C. Discussion.

1. Effect of Degree of Polymerization on Pattern.

The patterns which consist of snakelike regions covering only a small portion of the area of the surface are the result of using polymer with a low degree of prepolymerization, and final cure, and therefore with a low viscosity. Such a polymer is able to flow more effectively during cure, and can clump together more as shrinkage occurs, showing the effects of surface tension.

The fernlike patterns are probably regions in which wetting has proceeded effectively, and in which shrinkage during cure has caused some degree of corrugation, but in which a large portion of the polymer has remained as an adhesive between the two specimens. The specific shape finally shown after break appears to be related to occurrences during the break, and is being further investigated.

The outer ring around the fernlike patterns may be due to some extent to the effect of the nitrogen or oxygen of the atmosphere on the edges of the adhesive, or may be due to edge effects of the metal specimen.

The occurrences during break include: breaking loose of weak portions of the adhesive bond, a small amount of

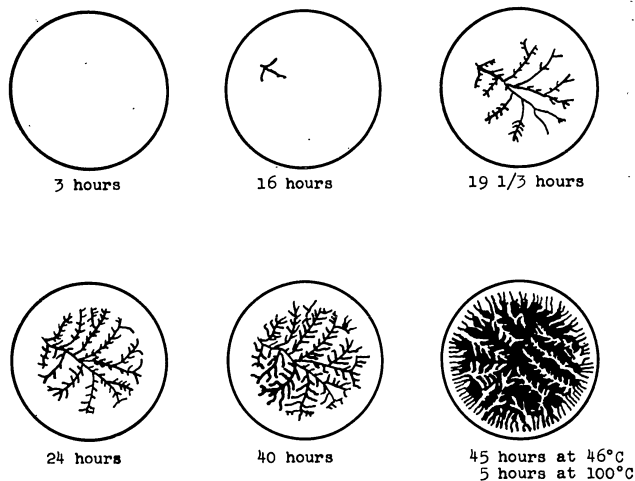


Fig. 2/ Progressive Development of the Fern Pattern in Adhesion Samples
Time of cure up to the moment of the pattern is shown.

plastic flow (smaller for the more fully polymerized material), corona-like electrical discharge from one sample to the other, and final effects of the atmosphere on the stripped metal, and its opposite polymer, after break. The relation between patterns and various ones of these occurrences during break is being further studied; in this connection reference is made to ref. 45, by the author and his colleagues on the detailed electrical phenomena occurring at the stripping of polyester adhesive from glass.

It should be reemphasized that the results of this section refer to the experimental results obtained with the polymethylmethacrylate adhesive only; of the adhesives used in this investigation this one is the one which has been brought to the point of greatest reproducibility, and therefore with respect to which this type of investigation is meaningful instead of being subject to the perturbing effects of various random variables.

An obvious line of attack on this problem is to make bonds between the metal specimens and glass, and study the appearance of the cured bond under the glass before break. This was done repeatedly. However, the degree of adhesion to glass was considerably smaller than to metal, and therefore there is a difference in the conditions under which cure is taking place. While some similarity has been found, there is sufficient difference in the appearance of metal-polymer-glass specimens and metal-polymer-metal specimens so that the latter are regarded at this time as only furnishing qualitative rather than quantitative information. Some indication has accumulated that the presence of the glass-polymer adhesion bond has an effect on the nature of the phenomena occurring at the metal-polymer interface. This has not been confirmed.

In Fig. 2/, there is shown a typical progression of the formation of pattern during the shrinkage of polymethylmethacrylate adhesive as seen through a glass sheet bonded to a copper specimen. The metal-polymer-glass specimens were cured in an oven after preparation by the procedure described above, and examined periodically for development of the pattern. The times of cure are indicated for each picture. In the last two pictures, a slight regression of, and channeling through, most of the outer ring by minute radial channels is observed; this occurs during the latter portions of the polymer cycle. Complete channeling of the outer ring is observed with the metal-polymer-metal surfaces, but an excess of polymer on the oversize glass plate may have suppressed it in the present case.

SECTION IX

MEASUREMENTS OF CHARGE ON THE SAMPLE AND RELATED ELECTRICAL EFFECTS

A. Measurement of Charge.

1. Derivation of Charge from the Trace Pattern.

The experimental setup in its simplest form is shown in Fig. 33. With this setup, the separating samples form a condenser with separating plates, and an increasing inhomogeneous dielectric, partly adhesive, and partly air. In the cases in which it may be expected that the electrostatic component of adhesion is of a significant magnitude, the charge is concentrated so near the surface (x_0 is a fraction of 10^{-7} cm) that it may be assumed to be on the surface of the adhesive. The voltage of the separating halves increases because of the decreasing capacitance of the condenser. If this were the only effect, it would be possible to simplify the calculations. However, if the resistance in the circuit is infinite, and therefore this becomes the only effect, the voltages would rise to such great heights that discharge of the charge on the adhesive and metal would occur into the atmosphere in a corona-discharge like type of breakdown of the atmospheric dielectric.

To increase the accuracy of measurement, and to maintain the heights of the voltage pulse within the range of the oscillograph face, it is desirable to put a finite resistance R in the circuit. This resistance permits leakage of the induced charge (or actual charge if the adhesive is conducting) through the external circuit, and thereby decreases the net effective charge on the adhesive during the time that separation is taking place. Thus the rise in potential from the decrease in capacitance is balanced by the lowering of potential which results from the decrease of charge on the condenser. Initially the former is dominant, and finally the latter. The experimental trace is therefore a rise and fall of potential, the location and height of the peak being dependent upon the resistance used.

The total charge passing through the external circuit is easily calculated as

$$q = \int Idt = \frac{1}{R} \int Vdt = \frac{K_1 K_2}{R} A.$$

Here q is the charge measured, I is the momentary current at any time, which rises and then decays to zero, A is the area of the trace of voltage against time, and K_1 and K_2 are scale factors converting the time scale and the voltage scale of the oscillograph into suitable values for the units in which q is expressed.

It should be noted that q is merely the charge which has passed through the external circuit.

2. Relation Between Measured Value of Charge and Actual Charge on Specimen Face.

The charge q may differ from the actual charge on the specimen face for several reasons. All reduce the measured charge below the actual charge on the specimen. They are: a) The induced charge is initially zero, since all lines of force from the charge on the adhesive pass directly to the opposite charge on the other metal adherend. As the two samples separate, the induced charge on the adherend to which the adhesive is still attached represents only a portion of the balancing charge. Even with the finite separation of a fraction of a centimeter reached immediately after break by the tensile machine, during the time when current flow is great enough to give a voltage distinguishable from background, there are still some lines of force which continue to go to the charge on the opposite adherend. The charge represented by these, does not pass through the external circuit unless the separation is carried to infinity. This difference between q and the actual charge is usually negligible in the experimental setup as used here.

b) The breaking off of a piece of the adhesive with the stripped metal surface carries with it the charge which was contained in it. Therefore the charges which are separating are smaller than the actual ones which were separated by the interface. This is obviously true for macroscopic films or specks of adhesive. It is true also if a thin film of subvisual thickness remains on the metal surface, and serves to reduce measured charge appreciably.

c) If a piece of the metal is carried over with the adhesive, its charge must also be subtracted from both charges, since it is no longer present on the metal surface, and on the adhesive surface neutralizes the opposite charge present there. Again this makes an appreciable reduction in measured charge.

d) Since q is the charge passing through the external circuit, any charge which transfers between the halves of the broken sample without passing through the external circuit is not measured. The chief one of these charges is the discharge which occurs during the break because of the breakdown of the air dielectric. Such corona-like discharges arise because of the increasing voltage on the equivalent separating condenser, and the fact that the initial gap is extremely small. Thus a potential of 1 volt across the gap when it has separated by 10^{-3} cm is 100,000 volts per cm. In the course of the work there have been obtained voltages up to 500 volts peak, so that considerable loss occurs during the separation of faces. In order to decrease this loss, smaller resistances may be used, but the smallness of the resistance used is limited by the voltage sensitivity of the oscilloscope and attached circuit, and the necessity for integrating the area without too great uncertainty from background effects.

The loss through atmospheric discharge constitutes a major fraction of the total charge which should have been measured. The fact that consistent values were obtained in WADC Technical Report 50-158 shows that the manner of losing the charge was a smooth function of the total charge, rather than implying that the total charge which was originally present was that shown there.

B. Effect of Varying the Resistance in the Measuring Circuit.

1. Relationship Between Resistance and Rise Time.

As the resistance is decreased, the time constant of the circuit is decreased, and the rise time decreases. As the rise occurs more rapidly (although the voltage measured has decreased because of its linear dependence on R), a greater portion of the charge on the samples has been neutralized by the flow of current between the samples at the time that the separation of the samples has become great enough to cause a discharge to occur. Therefore, there is less charge available to be lost during discharge. The rise time will be used as a criterion of this improvement in charge registration in the tables that follow.

2. Measured Charges.

In the break of the samples in air, representative results obtained by varying the resistance in the external circuit during the break of a succession of samples prepared by identical methods are given in Table VII, below.

Table VII

Polymethylmethacrylate Adhesive Broken in Air Computed Charge vs. Rise Time			
Metal	Trace Rise Time usec	Computed Charge from Trace Area, esu	Comments
Al	2.5	7.266	(1)
Al	2.5	7.798	
Al	13.3	5.369	(2)
Al	13.3	5.875	
Al	27.3	0.628	(3)
Al	27.3	0.644	
Al	27.3	2.219	(4)
Al	2.5	18.45	
Al	2.5	15.4	(5)
Ni	27.3	2.696	
Ni	27.3	2.596	(6)
Ni	27.3	24.7	
Ni	27.3	23.2	(7)
Cu	20.8	17.0	
Cu	27.3	21.9	

The measured values of charge densities in air at atmospheric pressure gave values such as the above, with a maximum of 24.7 esu, using copper, nickel, and aluminum, series of samples. It is evident that the total amount of charge obtained is dependent upon the rate at which the peak voltage is obtained, i.e. by the rate at which charge can be neutralized by flow through the external circuit before the distance of separation is reached at which air breakdown occurs. Numbers in comments refer to preparational series. No attempt was made to determine the actual charge per unit area, since the actual area stripped was difficult to integrate, and constituted only a fraction of the

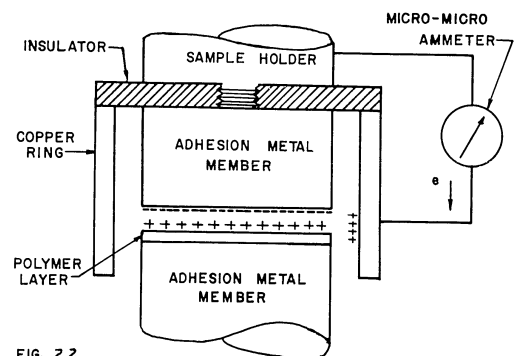


FIG. 2 2

1.2 cm² of the sample.

3. Verification of Loss of Charge By Air Breakdown.

The actuality of the loss of charge to the air was confirmed by placing a metal ring around the area of adhesion (but not touching either the metal or adhesive) and measuring the current flowing from it to one of the metal members. Fig. 22. The ring became charged the same sign as the polymer layer on the opposite adherend, i. e. oppositely from the metal member to which it was connected electrically. The geometry of the experiment precluded this being dominantly an induced charge. The current between the two lasted for only a fraction of a second.

In the literature, there is evidence for the emission of charge from such freshly broken surfaces into the atmosphere. In ref. 25, it was found that electrons with high energies were emitted from a freshly broken adhesive bond. In ref. 50, it was found that electrons with energies up to kilovolt magnitude were emitted from the freshly broken surface of a polymer cooling in a glass vial and breaking away from it.

To these references, should be added, of course, the experiments on the Russel and the Kramer effects which were mentioned in Sec. II.

C. Effect of Atmospheric Pressure.

1. Charge Values Reported in the Literature.

Krotova, Deryagin, Karasev, et al (7-9) have reported charge density values in vacuum of

1 x 10 ⁴ esu/cm ²	Gutta Percha - Glass
3 x 10 ³	Polyvinyl Chloride - Glass
8 x 10 ³	Cellulose Nitrate - Glass
4 x 10 ³	Cellulose Acetate - Glass
1 x 10 ⁴	Benzyl-Cellulose - Glass

Harper (19) measured charge densities as high as 8.7 x 10³ esu/cm² for very small contact areas at the contact between two spherical insulators. Rose and Ward (34) showed charge densities of 12 to 79 esu/cm² on various plastics from contact by metals and stated the charge values may be limited by discharge. Dawson (7) stated that the potential gradient between mercury and quartz after 20 second contacts was large enough to ionize gas. Adhesion of quartz and alkaline halide spheres moving relative to nickel spheres caused erratic results for Wagner (48) when the charge density had built up to 6 esu for 6 mm. diameter spheres.

2. The Paschen Curves.

The commencement of electrical breakdown of air during the discharge depends both upon the voltage attained by the faces, and upon the product of gas pressure and distance between the plates, by (6),

$$V \approx \frac{Bpd}{C + D \ln(pd)}$$

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Fig. 23 shows the dependence of required voltage upon the product $p d$. Since in these experiments the distance is increasing during the break, there will be a time in each break in which $p d$ reaches the value necessary to give discharge with the acceptable maximum voltages, except in very high vacuum.

3. Reduced Pressure Experiments.

High vacuum equipment was not available, and therefore, it was not possible to perform experiments duplicating the work of investigators named. However, it was possible to perform experiments in air at reduced pressures down to 5 x 10⁻³ mm. Hg. For this purpose, there was borrowed and utilized a vacuum chamber, constructed for another project, which was evacuated by for pump. The chamber is illustrated in Fig. 24/25. It consists of a sylphon wall, permitting mechanical movement during the tensile break, and still denying air entry. The top of the chamber is made from plexiglass with a metal center which connects to the support to the tensile machine and the bottom is brass through which the air entry and vacuum pump connection is made.

When the chamber with contained sample was inserted in the tensile machine and evacuated, it was necessary to apply a tensile stress of approximately 150 pounds to balance the air pressure. Additional force applied caused separation of the sample at its breaking stress.

The electrical connections were made to the top (insulated by Plexiglass, and to the bottom members, and through them to the sample. The same electrical circuit was used as in measurements in air. Table VIII shows typical results obtained.

Table VIII

Polymethylmethacrylate Adhesive Broken in Air at Reduced Pressure (.005 mm. Hg.)		
Metal	Trace rise time usec	Computed charge from area of trace esu
Al	2.52	2.15
Al	2.52	3.38
Al	2.52	4.05
Cu	2.52	5.84
Ni	0.28	9.16
Cu	0.28	17.0

It appears that the pressure must be still further reduced in order to avoid the loss of significant quantities of charge. Experiments at further reduced pressures were contemplated but could not be undertaken in the remaining period of the contract.

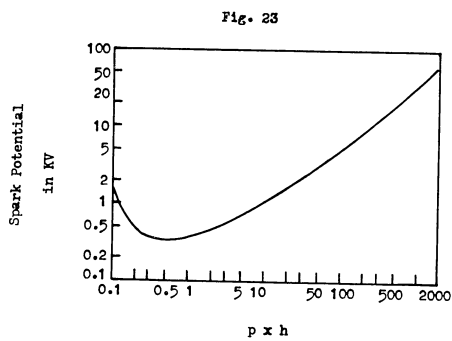
4. Correction for Discharge.

Various methods of correcting the measured charge for the effects of the atmospheric discharge were investigated with no unambiguous conclusion. This work is continuing.

69

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Paschen's law curve for air where p is the spark length in cm. and h is the density relative to density at 1 mm. Hg. and 20°C.

70

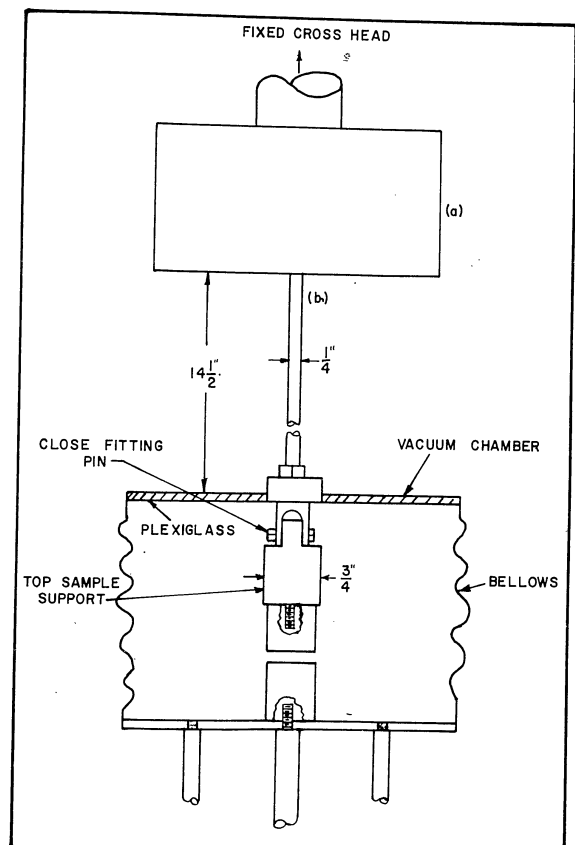


Fig. 24
71

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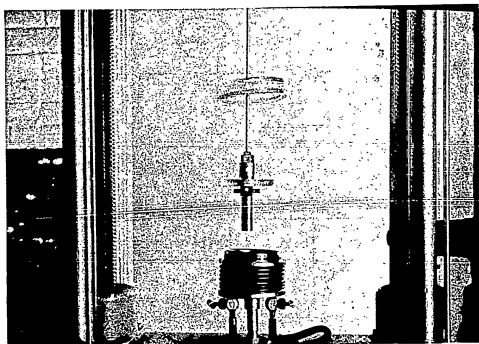
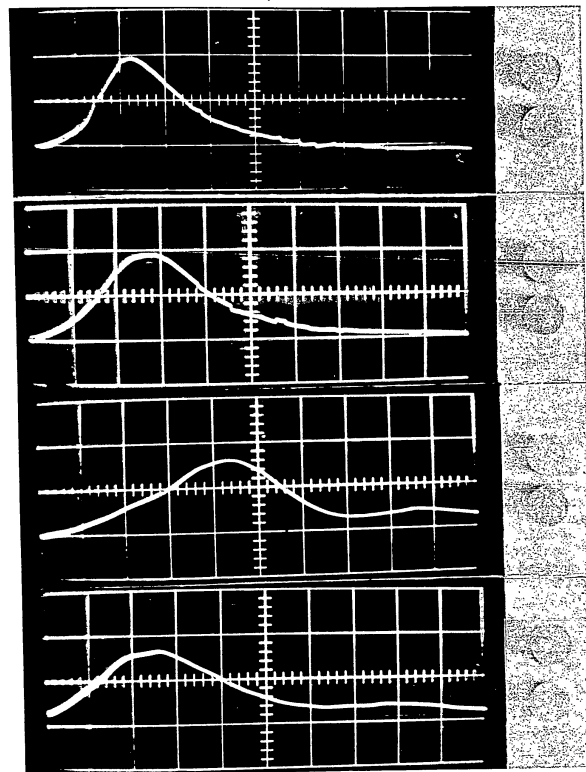


Fig.25 Vacuum chamber with sample mounted on the top part.



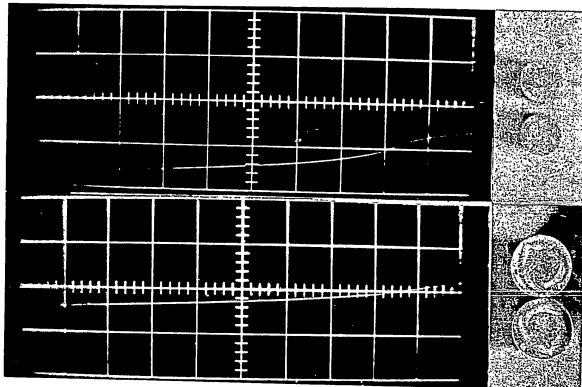


Fig. 26

Aluminum - PMMA samples of XO series showing good similarity of traces and surface patterns. The traces are a measure of the voltage across the sample by the cathode follower probe with 10X attenuator and 100K ohms. Samples in order, pressure at break, breaking strength, and integrated charge are:

	Breaking Strength	Pressure	Charge	Area
XO1	182	.06 mm.	3.38 esu	.231 cm ²
XO3	144	.04	4.05	.225
XO4	110	.02	2.15	.261
XO8	133	.04	2.36	.219
XO13	140	.15		
XO11	102	.16		

The second maximum in XO4 and XO8 is probably due to vibration of the mechanical system. Notice the dissimilarity in the polymer pattern on XO4 and corresponding difference in the trace with respect to the others. Traces XO13 and XO11 are 10 microseconds full scale, the others being 100 microseconds.

SECTION X

POSITION OF CLEAVAGE.

A. Theoretical.

1. Effect of Heterogeneity of the Metal.

In Appendix III, there is given a derivation of the effect of heterogeneity of the metal surface against which the adhesive is adhered. It is there shown that in the regions at which the energy barrier to the diffusion of charge into the adhesive is small, there will be a large charge transfer and therefore a strong adhesion. In regions in which the barrier is large, the diffusion of charge into the polymer, and the adhesion, will be much smaller. At regions with energy barriers between the large and small values, the charge transfer and resultant adhesion take intermediate values. Since the stressing takes place over the whole area of the specimen, it is resisted primarily by the more strongly adhering portions of the polymer. This does not necessarily mean that the weaker portions break away slowly during the stressing process, although this can happen, but it does mean that there is some degree of deformation of the plastic during the initial stressing.

2. Effect of Lateral and Internal Forces.

At the interface, there is a lateral force (of the type described by Faraday in terms of electrical lines and tubes of force) from the electrostatic charge. This is more commonly referred to as an electron (or hole) pressure inside the material, in the solid state point of view initiated by the developments of Sommerfeld and Fermi-Dirac, and the Pauli principle. This lateral force is equal in magnitude to the adhesive force. Similarly, according to the treatment in refs. 36 and 37, the electrical force urging the material towards the interface still exists in diminishing amount as the interior of the adhesive is approached; with it, there is also a decreasing lateral pressure. These lateral pressures can create strains, and particularly in a region immediately behind the differences in charge density at two adjacent regions, they can cause differences in stress which favor internal cracking. The force balance between all the applied forces and the forces evoked in the material as a result of its reaction to the applied forces, together with the electrical internal stresses, is therefore likely to produce fracture of the polymer in regions dependent upon the physical and electrical nature of adhesive and metal. It would appear unlikely that this fracture would uniformly occur at the exact interface (if one could be assumed to exist), between metal and polymer, since it is just at that region that the adhesive force is greatest.

3. Effect of Heterogeneity of the Polymer.

Heterogeneity of the polymer will introduce mechanical unbalances in a stressed specimen, and will predispose to regions which are weaker in breaking strength than nearby regions. Under stressing therefore, there will be regions, not necessarily at the interface, where the break will take place. In addition, there will be a separation of electrical charges between such regions in accordance with their electrical heterogeneity, and therefore differences of internal stressing from Maxwell forces. These, of course, constitute a portion of the overall internal stresses involved at break.

B. Experimental.

1. The Fractured Specimen.

When specimens are not specifically prepared to strip preferentially from one surface, microscopic examination of fractured specimens shows polymer in different regions on the two halves of the specimen, each matching the other. Rarely was there a case in which a smooth film was on both. This can be obtained with thick films of weak cohesion, but then cohesion of the adhesive rather than adhesion is being measured.

In general, with polymethylmethacrylate and polystyrene, the broken specimen showed polymer which consisted of surfaces of polymer like an alpine landscape. Different heights of polymer would follow each other in random fashion. However, the heights were not themselves random. Usually there were several well-defined heights, indicating a certain degree of crystallinity in the polymer, and favored depths of cracking. The tops of the different heights were roughly planar, and the depth differences were in the region from 10^{-3} to 10^{-2} mm. At the bottom, there was a section analogous to a sandy beach, with the metal surface corresponding to the water. It was often impossible to estimate the height at which this portion ceased.

2. The Use of Fluorescent Powders for Charge Identification.

When a mixture of two fluorescent powders of opposite charges was sprayed on the specimen immediately after break, as described in the previous report, the separate portions of positive or negative charge could be identified. Fig. 15 shows some such patterns. In a number of cases, the vertical portion of the fracture was charged oppositely from the flat portion between this and the next vertical portions; this was not always true, however. The powder permitted precise area measurements by photography, but the results of this type of analysis were inconclusive from the point of fracture mechanisms.

3. Submicroscopic Layers of Polymer.

Obviously, visual examination is unable to reveal layers of polymer on the metal below the thickness corresponding to the wavelength of the light used. Therefore, various chemical methods were used to detect polymer layers of smaller thickness. Results were again inconclusive. During this period, there was not available an electron microscope for photography.

After the work with the metal specimens was completed, it was possible to photograph some specimens of glass surfaces on which a polymeric layer had been bonded by means of the electron microscope. This was performed under other support and is being reported elsewhere, since the work of this contract was limited to adhesives on metal surfaces. However, a few typical photographs which bear on the question of the position of cleavage are available through the courtesy of the experimenter.* In Figs. 27, 28, 29, are shown three somewhat unusual transmission electron microscope photographs of silica replicas of broken surfaces, two being fractures of polymer only, and one being the surface

* Thesis M. T. Parker, Case Institute of Technology, 1957.



Fig. 28
Enlargement of Portion of Fig. 29



Fig. 27
Electron Microscope Photo of Polyester-Glass Interface After Break. Replica technique.

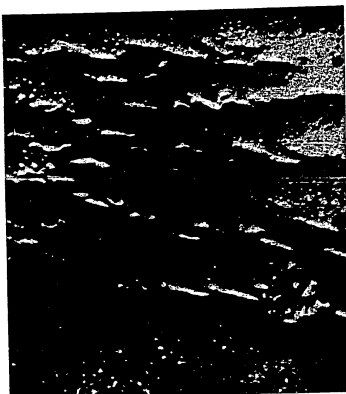


Fig. 29
Electron Microscope Photo of Inhomogeneity at Interface Between Glass and Polyester Adhesive

of a polymer layer after breaking away from the adherend. Fig. 29 is an enlargement of a portion of Fig. 28. The appearance of ridges on the polymer after breaking away from the adherend is particularly evident, even though fracture in the usual sense had not occurred.

C. Discussion.

Lebedev and Kuysinsky (24) noted that the fracture within polymethylmethacrylate took place in steplike surfaces having a parabolic or hyperbolic configuration. They attribute this cleavage to the propagation of very fine cracks from the center of the fracture in a direction transverse (perpendicular) to the direction of tension. The joining of converging cracks produce slips perpendicular to their surfaces. Their investigation was carried out using an interference microscope where the interference patterns represented height differences of 0.27 microns.

Patrick and Vaughn (34) have performed ellipsometer experiments which give strong indication that there is always a thin layer of polymer left on the metal surface whenever an adhesive break occurs.

If this is true, then the explanations of adhesion on the basis of dipole or dispersion forces from metal to polymer extending across the interface from adherend to adhesive become somewhat questionable. Short range forces would not extend into the polymer for great distances, and their effect would become rapidly weaker with depth. The explanation would have to consider such forces as between the different portions of the polymer itself, in which there is considerably less phase difference.

SECTION XI

DISCUSSION AND CONCLUSIONS

The purpose of this investigation has been to examine the effects which may be anticipated, or may be measurable, that will result from the presence of space charge in polymeric materials. The minimum number of assumptions have been used, and in this first approximation it has been assumed that such additional ad hoc assumptions as particular distributions of trapping energy levels, infinitely thin layers of charge or surface states, represent levels of complexity which are unnecessary to the theory. In ref. 43, it has been shown that the treatment on which the present work has been based can be extended to include trap distributions by the use of particular values for the dielectric constant, without other change. Here, the accepted basic experimental and theoretical results of solid state theory, classical and irreversible thermodynamics, and electrostatics, have been utilized to explain the behavior of insulating materials. One major result of the treatment has been the prediction that space charge will exist within an insulating material (and not just at the surface) in the vicinity of an interface with a material of different chemical nature.

The metal-polymer interface has been chosen as the representative of the theory primarily susceptible to experimental investigation. Extremely precise preparation and experimental techniques had to be developed to avoid the wide deviations in electrical and mechanical effects which result in this field from small traces of random chemical nature.

There have been examined the nature of the transfer across the interface, the adhesive force which results because of the charge transfer, the lateral force accompanying the adhesive force, the effect of heterogeneity in the polymer, the mechanical effects in the polymer of heterogeneity in the metal surface, the effects of fixed charge distribution in the polymer upon the mobile charge carriers and electrical field therein, and the position at which an adhesive bond will actually rupture. Experimentally, it was necessary to develop a number of precision methods of working with polymers in adhesive technology, sufficiently precise so as to avoid the wide deviation in electrical behavior which is observed with usual excellent adhesive technology; these are described in Sections IV and V. With these special methods, the preparation and measurement including breaking of some 20 samples required relatively continuous work on the part of from one to three people for several weeks; the sample is, of course, destroyed in the break and the process is then repeated for the next set of samples.

With samples prepared as described, it has been possible to study the effects of prepolymerization of styrene and methylmethacrylate upon breaking strength, the effects of various changes in preparational schedule (particularly a number of different methods of metal surface preparation) upon the breaking strength, and the effects of total cure time upon breaking strength, as well as examining the electrical effects. In this connection, there emerged evidence that the pattern taken by the polymethylmethacrylate as it shrinks during cure is related to the nature of its adhesion to the adherends. These subjects are discussed in Sections VI to VIII inclusive; final results have not yet been obtained for the patterns. The data obtained on the effects of metal surface preparation, and the effect of variation of polymerization schedule show definite relationships which can be utilized to obtain strong bonds with this polymer.

In the use of exceptionally pure material, it was observed that the metal of the adherend diffused through the polymer (which it did not do observably if the water content of the polymer was above 0.04 per cent). This diffusion, and the fact that the electrical space charge in the vicinity of heterogeneity of either metal or polymer favors breakage at other than the exact interface (if one exists), supports the data of others to the effect that ordinarily the breakage of an adhesive bond occurs within the adhesive and not at the metal-organic bond at the interface. However, this does not necessarily imply that the properties of the polymer at the position of cleavage are the same as those of the bulk polymer; the presence of the metal and the fact that electrostatic forces are long-range forces imply a modification of polymer properties in this region.

The conclusions from the experimental and theoretical work are given in appropriate sections. Since each refers to the particular conditions and model or experimental setup there described, their repetition here would require unwarranted space. The general conclusions, however, are that:

1. Space charge exists in polymeric materials in the vicinity of interfaces with chemically different materials. The extent to which it exists is dependent upon the relative chemical, and therefore solid state, properties of both materials, and upon the geometry of both materials.
2. Chemical properties of polymers may determine the presence of traps or fixed charge distribution. The qualitative way in which such limited charge mobility affects the properties here discussed is a combination of the results in Appendix II, and in ref. 43.

3. Space charge in polymers results in very definite modification of electrical and mechanical properties of the polymers. However, it does not render the polymer conducting, except in extremely thin films, since it decreases rapidly with distance from the interface.
4. The modification in adhesive strength which can be obtained by different surface treatments of the adherend is enormous. The effects of such surface treatments are presented and discussed in detail.
5. Not all the charge which is transferred between polymer and metal is measured by the technique used in the previous report. Instead, a major portion of it is lost to measurement through atmospheric breakdown during separation after break. The indicated charge increases as circuit resistance decreases, i.e., the more chance the charge has to pass through the external circuit before the potential across the broken bond reaches the value at which atmospheric discharge starts.
6. There is little likelihood of break of an adhesive bond without some retention of polymer on the metal member, or in cases of metal weakness of tearing out of some metal with the departing polymer.

To these should be added the separate conclusions in the various specific sections of the report.

Section XII

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APPENDIX I

THE THERMODYNAMIC EQUILIBRIUM OF FREE CHARGE IN A HETEROGENEOUS DIELECTRIC ADHESIVE BOND

1. Introduction.

The basic differential equation for the thermodynamic equilibrium of free charge in a dielectric utilizing solid-state concepts and irreversible thermodynamics is nonlinear, and therefore it is impossible to build up the solution for a particular case by the addition of particular solutions. Instead, it is necessary to find the correct solution for the particular boundary conditions, using the general types of solutions given in Section II, 4, of ref.36, and fixing the values of the arbitrary parameters to agree with the actual physical system under consideration.

The solutions there given are of three types, corresponding to the cases in which the parameter g^2 is more than, equal to, or less than zero. The first is the case of the finite dielectric between metal adherends of work functions which are not very different and may be identical. The second is the case of the infinite dielectric, and the third is the case of the finite dielectric between metal adherends of very different work functions. A finite slab of dielectric between two different metal or nonmetal contact interfaces may exhibit behavior corresponding to any one of the three solutions, depending upon the particular physical conditions. In the case which is important to consideration of the electrostatic component of adhesion, namely that in which a considerable amount of charge has been transferred between the metal adherend and the dielectric adhesive over the interface, both the first and the third solutions tend to approximate the solution for the infinite dielectric. This is fortunate, because this solution is a much less complex mathematical expression. In such cases, therefore, it is possible to use the infinite dielectric solution as a very good approximation to the actual case.

2. The Individual Solutions.

In each case, the solution is given by expressions of the type:

$$\begin{aligned} (\psi - \psi_0) &= 2kT \ln(M), \\ F &= -(2kT/e) N, \\ n &= (\epsilon kT/2qe^2) P, \end{aligned} \quad (1)$$

in which ψ is the electrostatic potential energy, i. e. the electrical potential multiplied by the charge of the electron e , F is the electrical field, ϵ is the dielectric constant of the material, M , N , and P , are the functions given below, and k and T are the Boltzmann constant and the absolute temperature respectively.

For the various cases,

	$g^2 > 0$	$g^2 = 0$	$g^2 < 0$ $a^2 = -g^2$
M	$\frac{\sin g(x+x_0)}{\sin g x_0}$	$\frac{x+x_0}{x_0}$	$\frac{\sinh a(x+x_0)}{\sinh a x_0}$
N	$g \cot g(x+x_0)$	$(x+x_0)^{-1}$	$a \coth a(x+x_0)$
P	$g^2 \csc^2 g(x+x_0)$	$(x+x_0)^{-2}$	$a^2 \operatorname{csch}^2 a(x+x_0)$

(2)

Within the dielectric, there may be a maximum in the electrical potential whenever g^2 is more than zero, and this case must be distinguished from the cases in all three types of solution in which the electrical potential is monotonic.

3. Fitted Solutions.

Obviously, a large number of possibilities arise in fitting together solutions of these types; however, the process is straightforward, and the only deterrent is mathematical complexity. The process may be illustrated by a single instance, and other types of relationship between the physical properties of the dielectrics in contact and the metal adherends can easily be derived by analogous treatments. The case to be illustrated is that of a metal adherend contiguous to one dielectric which is joined to another dielectric adhesive at a planar interface, the other adhesive being of finite extent also, and in contact on its opposite surface with a different metal. The system is shown in the figure. Since the case of large charge transfer is the important one technologically, it will be assumed that in both dielectrics the solution corresponding to $g^2 > 0$ is valid (i. e. that the work functions of the metals differ only slightly, and that the electrical properties of the two dielectrics are not too greatly different). Since in the single dielectric between identical adherends, there is a potential maximum at the center plane of the dielectric, it will also be assumed that there is a potential maximum within one of the two dielectrics. These restrictions and assumptions are merely restrictions on the particular set of boundary conditions which we choose to examine; out of all the possible combinations of boundary conditions, i. e. values of the various physical properties, a selection has been made. By successively changing the assumptions under which the treatment is derived, additional combinations of boundary conditions may be examined without overlap, and when the total of possible combinations of types of solutions has been examined, the total sets of boundary conditions will have been covered once and only once.

4. Boundary Conditions.

From solid state and electrical theory, appropriate boundary conditions are:

$$\left. \begin{aligned} x=0: \psi_1 = \psi_{01} = \phi_1 - x_1; n_{01} &= N_c \exp [(\phi_1 - x_1)/kT]; \\ x=D: \psi_2 = \psi_{02} = \phi_2 - x_2; n_{02} &= N_c \exp [(\phi_2 - x_2)/kT]; \\ x=d: \epsilon_1 F_1(d) = \epsilon_2 F_2(d); \psi_2 - \psi_1 &= x_1 - x_2; \end{aligned} \right\} (3)$$

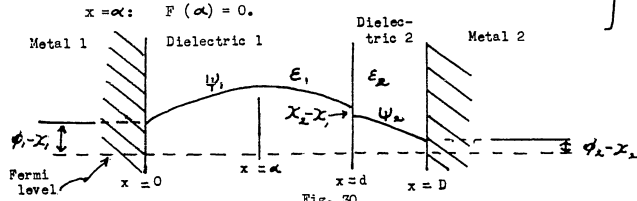


Fig. 30

Since the potential maximum may lie in either dielectric, $0 < \alpha \leq d \leq D$, and each case must be considered separately. The case considered below is that when the maximum is in the first dielectric.

5. Application of Boundary Conditions.

Consider first the case in which the maximum lies in the first dielectric (on the left). We define

$$\left. \begin{aligned} W &= \psi/kT \\ Y &= \frac{eF}{kT} \end{aligned} \right\} (4)$$

and designate quantities in the first dielectric by subscript 1, and in the second by 2. Then, here,

$$\left. \begin{aligned} x < d: W_1 &= \frac{\phi_1 - x_1}{kT} + 2 \ln \frac{\sin g_1 (x + x_{01})}{\sin g x_{01}} \\ Y_1 &= -2g_1 \cot g_1 (x + x_{01}) \\ n_1 &= n_{01} \csc^2 g_1 (x + x_{01}) / \csc^2 g x_{01} \\ x > d: W_2 &= 2 \ln \frac{\sin g_2 (D - x + x_{02})}{\sin g_2 x_{02}} + \frac{\phi_2 - x_2}{kT} \\ Y_2 &= +2g_2 \cot g_2 (D - x + x_{02}) \\ n_2 &= n_{02} \csc^2 g_2 (D - x + x_{02}) / \csc^2 g_2 x_{02} \end{aligned} \right\} (5 a, b)$$

The boundary conditions yield

$$\text{at } \alpha: F(\alpha) = 0, \quad g_1 = \frac{1}{2}(\alpha + x_{01}) \quad (6 a)$$

$$\text{at } d: \epsilon_1 g_1 \cot g_1 (d + x_{01}) = \epsilon_2 g_2 \cot g_2 (D - d + x_{02}) \quad (6 b)$$

$$\frac{\sin g_2 (D - d + x_{02})}{\sin g_2 x_{02}} \frac{\sin g_1 x_{01}}{\sin g_1 (d + x_{01})} = \exp \frac{\phi_1 - \phi_2}{2kT} \quad (6 c)$$

The conditions on at $x=0$ and $x=D$ have been incorporated in the expressions (5), and the three relationships (6) suffice to determine g_1 , g_2 , and α , in terms of the ϕ 's, the x 's, and the x_0 's. Knowing these expressions for g_1 , g_2 , and α , the values of x_0 are determined by the expressions (5) for the charge carrier densities at the interfaces. Equations (6) can be simplified somewhat as follows:

$$\text{Eq. (6 c) becomes } \frac{\sin g_2 (D - d + x_{02})}{\sin g_1 (d + x_{01})} = Q \frac{\sin g_2 x_{02}}{\sin g_1 x_{01}}, \quad (7 a)$$

and with Eq. (6 b) yields

$$\frac{\cos g_2 (D - d + x_{o2})}{\cos g_1 (d + x_{o1})} = \frac{\epsilon_1 g_1}{\epsilon_2 g_2} Q \frac{\sin g_2 x_{o2}}{\sin g_1 x_{o1}} \quad (7b)$$

Eqs. (5) and (3) yield

$$\frac{1}{\epsilon_1} 2 \left(\frac{2\pi e^2}{\epsilon kT} \right) N_c \exp \left[-(\phi_1 - \chi_1)/kT \right] = \csc^2 g_1 x_{o1}$$

$$\frac{1}{\epsilon_2} 2 \left(\frac{2\pi e^2}{\epsilon kT} \right) N_c \exp \left[-(\phi_2 - \chi_2)/kT \right] = \csc^2 g_2 x_{o2}$$

so that

$$\sin g_2 x_{o2} = g_2 \left[(2\pi e^2 / \epsilon kT) N_c \exp \left\{ -(\phi_2 - \chi_2)/kT \right\} \right]^{-\frac{1}{2}}$$

$$= \frac{S_2}{S_1}$$

$$\sin g_1 x_{o1} = g_1 \left[(2\pi e^2 / \epsilon kT) N_c \exp \left\{ -(\phi_1 - \chi_1)/kT \right\} \right]^{-\frac{1}{2}}$$

$$= \frac{S_1}{S_1}$$

so that

$$\frac{\sin g_2 x_{o2}}{\sin g_1 x_{o1}} = \frac{S_2}{S_1} = \frac{g_2}{g_1} \exp \left[-\frac{(\phi_1 - \chi_1) - (\phi_2 - \chi_2)}{2kT} \right],$$

and therefore (7a) and (7b) yield

$$\frac{\sin g_2 (D - d + x_{o2})}{\sin g_1 (d + x_{o1})} = \frac{g_2}{g_1} \exp \left(\frac{\chi_1 - \chi_2}{2kT} \right) = H$$

$$\frac{\cos g_2 (D - d + x_{o2})}{\cos g_1 (d + x_{o1})} = \frac{\epsilon_1}{\epsilon_2} \exp \left(\frac{\chi_1 - \chi_2}{2kT} \right) = J. \quad (9)$$

Eqs. (6a), (8), and (9) furnish the five relations necessary to evaluate x_{o1} , x_{o2} , g_1 , g_2 , and α . From (6a), g_1 is determined, and this substituted in the second of (8) yields x_{o1} . From the first of (8), x_{o2} is evaluated in terms of g_2 . All these are substituted in either of (9), and g_2 is determined. All four of these quantities now depend only on known physical property values, and on the value of α . Substitution in the other of (9) therefore determines the value of α . The requirement that α lie within the first dielectric imposes conditions on the possible values of the physical properties which are under consideration.

6. The Case of Appreciable Charge Transfer at the Metal-Dielectric Interfaces.

Taking up the case described in Sec. 3, we have the simplifying facts that

$$x_{o1} \ll d, \quad x_{o2} \ll D - d, \quad \text{and that}$$

$$|\phi_1 - \phi_2| < kT, \quad |\chi_1 - \chi_2| < kT.$$

Therefore, g_1 are of the order of $\frac{\pi}{2}$ and $g_1 x_{o1} \ll 1$. Also, in most plastics, the dielectric constant is in the range from 2 to 4, and for rough purposes, we may assume that $\epsilon_1 = \epsilon_2$. With these simplifications,

$$g_1 = \pi/2 \quad (\alpha + x_{o1}) ; \quad x_{o1} = S_1/g_1 = \frac{(\alpha + x_{o1}) S_1}{\pi} \quad (10)$$

Also $x_{o2} = S_2/g_2$, and (9) become

$$\frac{\sin [g_2 (D - d) + S_2]}{\sin (\pi d/2\alpha)} = H,$$

$$\frac{\cos [g_2 (D - d) + S_2]}{\cos (\pi d/2\alpha)} = J,$$

$$\text{so that } 1 = H^2 \sin^2 (\pi d/2\alpha) + J^2 \cos^2 (\pi d/2\alpha),$$

$$\text{and } g_2 = g_1 \left[\left\{ \exp \left(\frac{\chi_2 - \chi_1}{kT} \right) - \left(\frac{\epsilon_1}{\epsilon_2} \right)^2 \cos^2 \left(\frac{\pi d}{2\alpha} \right) \right\} \csc^2 \frac{\pi d}{2\alpha} \right]^{\frac{1}{2}} \quad (12)$$

If the second dielectric is thin compared to the first, and appreciable charge transfer occurs

$$x_{o1} = \left\{ (2\pi e^2 / \epsilon kT) N_c \exp \left[-(\phi_1 - \chi_1)/kT \right] \right\}^{-\frac{1}{2}} \alpha d, \quad (13)$$

$$x_{o2} = \left\{ (2\pi e^2 / \epsilon kT) N_c \exp \left[-(\phi_2 - \chi_2)/kT \right] \right\}^{-\frac{1}{2}} \alpha (D - d),$$

$$g_1 = \frac{\pi}{2\alpha} = \exp \left(\frac{\chi_1 - \chi_2}{kT} \right) \cdot \frac{\sin \pi d}{2\alpha}$$

and $D - d \ll D$,

so that

$$\frac{\pi(D-d)}{2\alpha} \left[1 + \cos\left(\frac{\pi D}{2\alpha}\right) \cdot \exp\left(\frac{x_1 - x_2}{kT}\right) \right] = \sin\left(\frac{\pi D}{2\alpha}\right) \cdot \exp\left(\frac{x_1 - x_2}{kT}\right)$$

from which if $D/2\alpha = 1 + \gamma$ where $\gamma \ll 1$,

$$\gamma \approx -\frac{(D-d)}{2\alpha} \frac{(x_1 - x_2)/kT}{1 - (x_1 - x_2)/kT} \quad (14)$$

$$\text{Therefore } \alpha \approx \frac{D}{2} + \frac{D-d}{2} \frac{(x_1 - x_2)/kT}{1 - (x_1 - x_2)/kT} \quad (15)$$

$$\frac{D}{2\alpha} = 1 - \frac{(D-d)}{D} \frac{(x_1 - x_2)/kT}{1 - (x_1 - x_2)/kT} \quad (16)$$

7. Discussion.

As would be expected the potential maximum is midway between the two metal adherends if either there is no physical difference between the two dielectrics, or if one dielectric extends the whole way between the two metals. If the conduction level of the second dielectric is higher than that of the first ($\alpha_2 < \alpha_1$), the potential maximum shifts toward the second dielectric, and if the reverse is true, it shifts in the other direction. This is because a higher conduction level in the second dielectric requires the potential to climb to a higher maximum in the first dielectric in order to have suitable charge equilibrium at the dielectric-dielectric interface.

The various quantities of physical interest may all be computed from the expressions derived above. Of these, probably the one of the greatest interest is the effect on electrical field at the boundary, $x = 0$. In this case, since equal charge densities or $(\phi - \chi)$'s at the metal boundary must be assumed for the case of the identical and the case of two different dielectrics, the cotangent terms must be identical. Therefore, the ratio of the boundary field in the two dielectric case to that in the single dielectric is

$$\frac{F_{11}/F_1}{D/2\alpha} = 1 - \frac{(x_1 - x_2)/kT}{1 - (x_1 - x_2)/kT} \cdot \frac{(D-d)/D}{1 - (x_1 - x_2)/kT},$$

which decreases as the conduction level in the second dielectric rises, and for a given $x_2 > x_1$, increases as the plane between the two dielectrics approaches the plane $x = 0$.

The expressions must not, of course, be interpreted in regions in which the approximations made are invalid.

The force of adhesion at the first metal boundary being proportional to F^2 will therefore increase if the second dielectric is one of lower conduction level, and decrease if it is of higher conduction level. In the latter

case, increase of thickness of the second dielectric will reduce the amount by which the electrostatic component of adhesion has been lowered.

APPENDIX II.

THE EFFECT OF FIXED CHARGE DISTRIBUTION IN AN INSULATOR UPON THE FREE CHARGE DENSITY, AND THE ELECTRICAL FIELD WITHIN THE INSULATOR.

1. The Fundamental Equations.

As in Reference 34, it is assumed that the charge which is free to move in the dielectric obeys the solid state current equations,

$$j = \sigma F - eD \frac{dn}{dx} = ne\mu F - bkT \frac{dn}{dx}, \quad (1)$$

i. e. that the observed current consists of the sum of the current resulting from the action of the electric field upon the free charges, and the current resulting from diffusion away from regions of higher concentration of charge into regions of lower charge concentration. The latter current is not primarily dependent upon the charge on the carrier nor the local field, and therefore the diffusion component depends only upon the local concentration of free charges, not on that of fixed charges.

At the zero-current, static, equilibrium, therefore,

$$y = \frac{eF}{kT} = \frac{d(\ln n)}{dx}. \quad (2)$$

By Poisson's Equation, the gradient of the electrical field is related to the total charge density (including fixed charge) by

$$\frac{dF}{dx} = \frac{4\pi e}{\epsilon} (n + N - P), \quad (3)$$

in which n is the free charge carrier density, and N and P are the concentrations of units of fixed negative and positive charge respectively. Equations (2) and (3) yield the expressions:

$$\frac{hve^2}{\epsilon kT} (N - P) = \frac{dy}{dx} - \frac{1}{y} \frac{d^2 y}{dx^2}, \quad (4)$$

$$\frac{hve^2}{\epsilon kT} n = \frac{dy}{dx} - \frac{hve^2}{kT} (N - P). \quad (5)$$

The equation is nonlinear, and difficult to solve for any but fortunate choices of the number of fixed charges as a function of distance; a constant density of fixed charges yields an equation in terms of non-tabulated functions. However, considerations of thermodynamic equilibrium indicate that in the vicinity of an interface, it would not be expected that the density of fixed charges would be a constant independent of spatial coordinates. The equilibrium state is reached by a complex set of electronic, atomic, and ionic diffusions and interactions, and although the mobility of ions is considerably smaller than that of electrons, nevertheless, there should be a gradual transition ionically and atomically from the state characteristic of the vicinity of the interface to that characteristic of the interior of the unperturbed dielectric. Therefore, a representative mathematical treatment will be given which while precise, may be regarded as a qualitative approximation to the actual physical behavior in the vicinity of an interface when fixed charges arise in the dielectric. The field term y will be specified and the corres-

ponding distributions of n and N will then be examined. Only the dielectric extending to infinity in one direction will be taken up.

From existing solid state theory, it is evident that the electrical field will beyond some depth decrease from the value characteristic of the interfacial region, as the interior of the polymer is approached. Furthermore, as the interior is approached, i. e. as x becomes large, charge densities will decrease, and neither n nor $(N - P)$ will become large without bound; n , at least, will decrease to a value related to the characteristic of the intrinsic energy gap of the material, as modified by the presence of fixed charge.

Therefore, such mathematical expressions as those listed below are unsuitable as describing the electrical field, F , or the variable y , for the reasons shown:

$$y = Ax^m, Ae^{+bx}, Ax^m + bx^2$$

electric field does not decrease towards the interior;

$$y = +Ax^m e^{-bx^2}$$

both n and $N - P$ have a term proportional to x^2 , and therefore increase without limit towards the interior.

2. Solution.

The expression which will be chosen is

$$y = -Ax^m e^{-Bx} \quad (6)$$

in which m may be positive or negative but A and B must both be positive. Here x stands for $(x + x_0)$ so that the interface is $x = x_0$. For this particular assumption, there are obtained:

$$\begin{aligned} F &= -\frac{kT}{e} Ax^m e^{-Bx} \\ n &= \frac{\epsilon kT}{hve^2} \left[\frac{n(m-1)}{x^2} - \frac{2mB}{x} + B^2 \right] \\ N - P &= \frac{\epsilon kT}{hve^2} \left[-A \left(\frac{m}{x} - B \right) x^m e^{-Bx} - \frac{n(m+1)}{x^2} + \frac{2mB}{x} - B^2 \right] \end{aligned} \quad (7)$$

$$\begin{aligned} \rho &= e[n + N - P] = \frac{\epsilon kT}{hve^2} A \left(B - \frac{m}{x} \right) x^m e^{-Bx} \\ &= \frac{\epsilon}{h\pi} \left(\frac{m}{x} - B \right) F \end{aligned}$$

If m is positive, the field rises to a maximum and then decreases exponentially with increasing x ; whereas, with negative m , the field decreases from the interface into the dielectric. At large distances into the dielectric, the free and fixed charge densities are equal in magnitude and opposite in sign, as would be expected for neutrality of the unperturbed dielectric. If this is considered to correspond with the case of fixed donors in solid state theory, at not too high temperatures,

$$\frac{\epsilon kT}{4\pi e^2} B^2 = n = (N_d N_c)^{1/2} \exp(-\delta/2kT), \quad (3)$$

where N_d is the concentration of donors, i. e. $= N$, and δ is the energy gap between the donor levels and the conduction level; in this case, if there is no positive fixed charge, the concentration of donors must be given by

$$N_d = N_c \exp(-\delta/kT),$$

and, in general, the concentration of fixed positive charge corresponding to this particular situation is

$$P = N \left[1 + \sqrt{(N_c/N) \exp(-\delta/kT)} \right]$$

For positive m , the requirement that the free charge density be positive fixes minimum limits on x (which stands for $(x + x_0)$), and since the interface is at $x = x_0$, imposes limits on the characteristic quantity, x_0 . From the development in Ref. 36, this means that the present discussion is, for positive m , limited to interfacial charge densities below a fixed amount which depends upon the value of m , but not limited for negative m .

3. Discussion of Particular Cases.

From Eq. (7), it is obvious that the model chosen yields the desired zero net charge in the interior of the dielectric, and that this corresponds to the existence of negative free charge density just sufficient to balance the net fixed charge density.

Several particular cases are worth considering:

1) $B = 0, m = -1$. In this instance, the fixed and free charge densities are:

$$N - P = \frac{\epsilon kT}{4\pi e^2} \left(\frac{A-2}{x^2} \right) \quad (9)$$

$$n = \frac{\epsilon kT}{4\pi e^2} \frac{1}{x^2}$$

and if A is equal to 2, the fixed charge density vanishes and the field is that given by the original solution. If A has any other value, the electrical field is

$$F = -\frac{AkT}{e} \frac{1}{x} \quad (9.1)$$

Accordingly, a different value of the electrical field showing the same rate of decrease into the interior of the dielectric corresponds to a fixed charge concentration showing the same functional decrease with distance as the free charge.

2) $B = 0, m = 0$. In this case, both the free charge density and the fixed charge density vanish, since the field is constant.

3) $B = 0, m = 1$. The free charge density vanishes, but there is a uniform concentration of fixed charges in the interior of the dielectric, and the electrical field increases proportionally to the distance. Similarly, any positive value of m is unrealistic.

4) $B \neq 0, m = 0$. The electrical field shows a simple exponential decrease towards the interior of the material; the free charge density is constant, and the fixed charge density decreases exponentially to a value equal in magnitude and opposite in sign to that of the free charge.

5) $B \neq 0, m = 1$.

$$F = -\frac{kT}{e} A x e^{-Bx}$$

$$N - P = \frac{\epsilon kT}{4\pi e^2} \left[-A(1 - Bx) e^{-Bx} + \frac{B}{x} - B^2 \right]$$

$$n = \frac{\epsilon kT}{4\pi e^2} \left[B^2 - \frac{2B}{x} \right]$$

$$P = \frac{\epsilon kT}{4\pi e^2} A(1 - Bx) e^{-Bx}$$

The free charge density can only be positive, and therefore $Bx_0 \geq 2$. Accordingly, the total charge density, ρ , is never of the same sign as the free charge, and decreases gradually to zero. Although it would appear that the electrical field can rise to a maximum and decrease, the limitation on x ensures that the field decreases in magnitude with increase of x , at all points.

6) $B \neq 0, m = -1$.

$$F = -\frac{kT}{e} A \frac{e^{-Bx}}{x}$$

$$n = \frac{\epsilon kT}{4\pi e^2} \left[\frac{2}{x^2} + \frac{2B}{x} + B^2 \right]$$

$$N - P = \frac{\epsilon kT}{4\pi e^2} \left[A \left(\frac{1}{x^2} + \frac{B}{x} \right) e^{-Bx} \right.$$

$$\left. - \frac{2}{x^2} - \frac{2B}{x} - B^2 \right] e^{-Bx}$$

$$\rho \propto \left(B + \frac{1}{x} \right) \frac{e^{-Bx}}{x}$$

The free charge density decreases as the interface is left behind, as does the electrical field. The total charge is also of the same sign as the free charge density and decreases rapidly to zero.

Other cases may be examined but do not add anything to the qualitative conclusions which may be drawn from the above.

4. Physical Significance.

The characteristic situation which requires consideration is that in which some of the free charge in the free thermodynamic equilibrium becomes fixed, nearer to the interface than it would be under free equilibrium. For this, the last solution discussed is characteristic. In the free case, the charge density would be

$$n = (\epsilon kT/2pe^2)x^{-2},$$

and the electrical field,

$$F = -(2kT/e)x^{-1}.$$

Here the total charge density is

$$(n + N - P) = (\epsilon kT/2pe^2)x^{-2} \left[\frac{A}{2} (1 + Bx)e^{-Bx} \right]$$

in which x has been substituted for $(x + x_0)$, and similarly the electrical field is

$$F = -\frac{kT}{e} A (x^{-1}) (e^{-Bx}).$$

The additional factors on the right in both cases cause a rapid decrease of the field and charge density as compared to the case of free charge. As the exponential coefficient B increases, the charge density is concentrated more and more nearly at the interface, and the field becomes smaller and smaller at a given distance into the dielectric. In the limit, the charge density is primarily a surface charge, and the field is nonexistent except at the immediate interface, where $x = x_0$.

In the interior of the dielectric, the free charge and fixed charge are finite and not zero, but cancel each other to yield zero net charge. The total charge density is everywhere the same sign as that of the free charge, since the free charge is always greater than the fixed charge, the excess increasing as the interface is approached. The fixed charge itself is all of one sign if A is less than 2, and changes from positive in the interior to negative near the interface, if A is more than two and Bx_0 is small.

5. Conclusion.

The analysis indicates that if there is fixed negative charge within the dielectric, instead of a completely free set of negative charges, thermodynamic equilibrium is attained with:

- 1) a more rapid decrease of field away from the boundary,
- 2) a more rapid decrease of total charge, and of free charge density,
 - i. e. concentration of the charge density nearer to the interface,
- 3) existence of free charge in the interior of the (unperturbed) material in sufficient quantity to neutralize any fixed charge there,

- 4) immobility of the fixed charge, and dynamic (diffusion) equilibrium of the free charge,

- 5) in the case where all quantities depend upon x only, no change in the value of the electrostatic component of adhesion (as described in the text and as determinable from the results here presented).

Similar considerations in the case of curved equipotential surfaces will make it qualitatively evident that concentration of the charge towards the interface will increase or decrease the electrostatic component of adhesion where the interfacial surface is characterized by curvature. These will be taken up elsewhere.

Appendix III

THE NATURE OF THE ADHESION AT A HETEROGENEOUS METAL SURFACE

A. The Charge Density at the Adhesion Boundary between a Plastic and a Heterogeneous Metal.

1. The Metal Surface.

Metals commercially used in adhesion bonds are neither single crystals, nor highly purified. Thus, oxygen-free copper is difficult to work because it sticks to tools; the copper used for routine machine-work is an alloy so compounded that in addition to other suitable properties it can be satisfactorily machined. Therefore, in addition to the presence of grains and grain boundaries on the surface, there is a varying work function characteristics of the particular local micro region in question, its chemical and crystallographic nature, and the amount of working it has received. In addition to this, there are adsorbed on the metal varying quantities of material which depend upon the history of the specimen. Even if the plastic were completely homogeneous and therefore had a constant electron affinity, χ , over its surface at the interface, the barrier energy, $\phi - \chi$, would vary from point to point.

2. The Interfacial Charge Density as a Function of Location.

Since the charge transferred in equalizing the Fermi levels in the adherend and the adhesive is determined by the barrier energy at the boundary, by the expression

$$n_0 = N_c \exp \left[-(\phi - \chi) / kT \right], \quad (1)$$

a change in $\phi - \chi$ will make a large change in n_0 . The charge density at the boundary, and the value of the characteristic quantity x_0 in the case of the infinitely extended dielectric are given in the Table. The total charge which has entered the adhesive per unit area is $n_0 x_0$; the number of electronic charges $n_0 x_0$ is also listed.

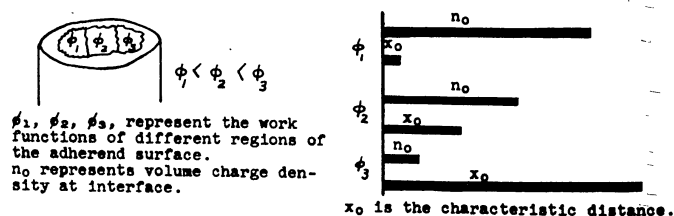


Fig. 31 The Effects of Surface Heterogeneity

Table IX

Effect of Barrier Energy on Boundary Volume Charge Density, Characteristic Distance, and Total Carriers Penetrating Interface Per Unit Area

Barrier height $\phi - \chi$, ev	Volume charge density n_0 (cm^{-3})	x_0 (cm)	$n_0 x_0$
2.0	6×10^{-15}	1×10^9	2.4×10^{-5}
1.5	2×10^{-6}	2.7×10^5	5.4×10^{-1}
1.0	1×10^2	1.7×10^1	6.8×10^3
0.8	9.1×10^5	3.5×10^{-1}	3.2×10^5
0.6	2.1×10^9	7.4×10^{-3}	1.5×10^7
0.4	4.8×10^{12}	1.5×10^{-4}	7.2×10^8
0.3	2.3×10^{14}	2.2×10^{-5}	5.1×10^9
0.2	1.1×10^{16}	3.2×10^{-6}	3.5×10^{10}
0.1	4.9×10^{17}	4.8×10^{-7}	2.3×10^{11}
0.075	1.4×10^{18}	2.9×10^{-7}	4.1×10^{11}
0.05	3.5×10^{18}	1.8×10^{-7}	6.3×10^{11}

In the table it is assumed that the dielectric constant of the plastic is 4. The maximum value of $n_0 x_0$ listed (computed in practical units) is almost exactly 10^{-7} coulombs, and the minimum value listed is about 4×10^{-24} coulomb. If the barrier height were that of the work function of copper, n_0 in vacuum would be less than 10^{-10} electrons / cm^3 and $x_0 > 10^9$, so that $n_0 x_0$ would correspond to 10^{-41} coulombs. This rather unrealistic value indicates that it is not surprising that at ordinary temperature there is no observable electron atmosphere outside copper in a vacuum. With increase of temperature, the effective barrier energy is decreased in the ratio of the ratio of increase of temperature, and there is a rapidly increasing development of an electron atmosphere, as may be seen from the table.

With a varying ϕ over the metal surface, therefore, there will normally be a varying density of charge transferred at the interface. The effect of this difference in charge density at the surface will be examined below.

B. The Expression for the Electrostatic Component of Adhesion in a Finite Sample.

1. The Finite Solution.

The solution of the electrostatic equations in ref. 37 shows that for a dielectric between two identical adherends

$$\left. \begin{aligned} F &= -\frac{2kT}{e} \kappa \cot g(x + x_0) \\ n &= \frac{e\kappa}{2\pi e^2} g^2 \csc^2 g(x + x_0) \end{aligned} \right\} \quad (2)$$

where $g = \pi / (D + 2x_0)$.

By the electrostatic equations, the force at the boundary, urging the adherend and adhesive towards each other is

$$f = \frac{\epsilon F^2}{8\pi} \quad (3)$$

In these equations, F refers to the electrical field, n to the volume charge density at any point in the dielectric, ϵ to the dielectric constant, D is the thickness of the adhesive, and x_0 is the characteristic quantity listed in the Table just above. The quantities k , T , and e , have their usual meaning. The values of x_0 are obtained from n in Eqs. (2), at the boundary, $x = 0$, using the known value of n_0 .

Using these expressions, it may be computed that

$$f = n_0 kT - \frac{\epsilon k^2 n^2}{2\pi e^2} \frac{\pi^2}{(D + 2x_0)^2} \quad (4)$$

For the average thicknesses of adhesion samples encountered in practice, D must be at least 10^{-3} cm, so that the last term in (4) is negligible at ordinary temperatures, in those cases in which a non-negligible electrostatic force exists.

2. The Actual Adhesive Bond.

The adhesive bond is commonly visualized as two adherends with accurately plane surfaces separated by a layer of adhesive of uniform thickness. Omitting consideration of the effects of chemical interaction at the interfaces, which itself is undoubtedly important in the practical case, it is still true that this is an idealized picture. In practice, the thickness of the adhesive must vary in accordance with micro-roughnesses of the metal surfaces. Also in the preparation of the metal surface, again in the practical case, there will undoubtedly be produced portions of the metal which are nearly torn off, or bent up, etc., which will cause differences of thickness of the adhesive. These also will be neglected in what follows, although they bring about the possibility of local values of D which are quite small.

Here, therefore, there will be considered completely planar adherends and uniform thickness adhesive; the conclusions reached must therefore be extended in practice to take account of the actual state of affairs.

3. The Characteristic Quantity x_0 .

Since x_0 varies over such a large range (from atomic dimensions to astronomic dimensions), as the charge density at the boundary decreases from a large value to a very small value, it is desirable to examine the extent to which the last term in Eq. (4) can really be neglected. This depends not only on whether the last term itself is small, but on the relative magnitudes of both terms. As x_0 becomes larger, n_0 decreases, so that the decrease of the last term is accompanied by a decrease in the first term on the right of the equation. To examine this it is useful to obtain a different expression for the mechanical force, and consider it in the limiting cases of large and small x_0 , i. e. in the cases of small and large charge density at the interface, corresponding to large and small values of the energy barrier.

4. The Force of Adhesion.

From (2) and (3), there are obtained

$$\begin{aligned} f &= \frac{\epsilon k^2 n^2}{2\pi e^2} g^2 \cot^2 g x_0 \\ n_0 &= \frac{\epsilon kT}{2\pi e^2} g^2 \csc^2 g x_0 \\ g &= \frac{\pi}{(D + 2x_0)} \end{aligned} \quad (5)$$

These will be used for the discussion to follow.

C. The Limiting Values of the Adhesion.

1. The Adhesion in the Case of Low Energy Barrier, and Consequent Large Transfer of Charge.

In this case, $x_0 \ll D$, and the expressions in Eq. (5) become, using standard approximation techniques:

$$\begin{aligned} g &= \frac{\pi}{D} \left[1 - \frac{2x_0}{D} \right] \\ f &= \frac{\epsilon k^2 n^2}{2\pi e^2} \frac{1}{x_0^2} \left[1 - \frac{2\pi^2 x_0^2}{3D^2} \right] \\ n_0 &= \frac{\epsilon kT}{2\pi e^2} \frac{1}{x_0^2} \left[1 + \frac{\pi^2 x_0^2}{3D^2} \right] \\ \therefore f &= n_0 kT \left[1 - \frac{\pi^2 \epsilon kT}{2e^2 n_0} \right] \end{aligned} \quad (6)$$

It is apparent, therefore, that in the case of the finite adhesion sample, the mechanical force on the adhesive will be somewhat less than $n_0 kT$, the ratio increasing, toward $n_0 kT$, however, as the barrier energy becomes smaller and n_0 increases.

2. The Adhesion in the Case of Large Energy Barrier, and Low Charge Transfer.

Here, $x_0 \gg D$, even for sizable values of D , and the expressions in Eq. (5) become:

$$\begin{aligned} g &= \frac{\pi}{2x_0} \left[1 - \frac{D}{2x_0} \right]; \quad g x_0 = \frac{\pi}{2} - \frac{\pi D}{4x_0}; \\ \cot g x_0 &= \tan \frac{\pi D}{4x_0}; \quad \csc g x_0 = \sec \frac{\pi D}{4x_0}; \end{aligned}$$

$$f = \frac{\epsilon k^2 T^2}{2 \pi e^2} \left(\frac{\pi^2 D}{4 x_0^2} \right)^2 \left[1 - \frac{D}{2 x_0} + \left(1 + \frac{\pi^2}{12} \right) \frac{D^2}{4 x_0^2} \right]^2$$

$$n_0 = \frac{\epsilon k T}{2 \pi e^2} \left(\frac{\pi^2}{2 x_0} \right)^2 \left[1 - \frac{D}{2 x_0} + \left(1 + \frac{\pi^2}{8} \right) \frac{D^2}{4 x_0^2} \right]^2$$

Using only the first and second approximation,

$$\therefore f = \frac{e^2 D^2 n_0^2}{2 \epsilon} \cdot \left[1 - \frac{\pi^2 e^2 D^2 n_0}{k T} \right] \quad (7)$$

which increases with n_0^2 , but does not increase so rapidly as does the first term.

3. The Adhesion in the Case of Intermediate Energy Barrier and Medium Charge Transfer.

Here, $2 x_0 \approx D$, and the expressions become

$$e x_0 = \pi / 4;$$

$$f = \frac{\epsilon k^2 T^2}{2 \pi e^2} \frac{\pi^2}{4 D^2}$$

$$n_0 = \frac{\epsilon k T}{2 e^2} \frac{2 \pi^2}{4 D^2}$$

$$\therefore f = n_0 k T / 2.$$

4. The Average Force Per Particle.

The total number of particles which have penetrated through unit area of the interface are

$$\int_0^{D/2} n dx = \frac{\epsilon}{4 \pi e} \int_0^{D/2} dF = \frac{\epsilon F_0}{4 \pi e}$$

In the cases in question, therefore, the number of charges passing through unit area of the interface were

$$D \gg x_0 : \sigma = n_0 e x_0 = (\epsilon k T n_0 / 2 \pi)^{1/2}$$

$$D \approx 2 x_0 : \sigma = (n_0 e k T / \pi)^{1/2} \quad (8)$$

$$D \ll x_0 : \sigma = n_0 e D.$$

Therefore, the average force per particle which has passed through the interface is

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$D \gg x_0 :$

$$f / \sigma = (2 \pi n_0 k T / \epsilon)^{1/2} = 2 \pi \sigma / \epsilon$$

$$D \approx 2 x_0 : f / \sigma = (k T / e) (\pi / 2 D) = \pi \sigma / \epsilon \quad (9)$$

$$D \ll x_0 : f / \sigma = e^2 n_0 D / 2 \epsilon = e \sigma / 2 \epsilon,$$

as is well-known from electrostatic theory.

D. The Adhesion at the Interface.

1. Relative Adhesion at Highly and Poorly Charged Surfaces.

The electrostatic component of adhesion is proportional to the square of the charge density at the boundary, for small total charge transfer (large barrier) and to the first power of n_0 for large total charge transfer. Therefore, if the total observed charge from the break of an adhesive bond corresponds to a uniform charge, the measured adhesion should be less than if the same charge corresponds to a distribution of different densities of interfacial charge. For example, suppose that 48% of the area has a charge density of 3.5×10^{10} electrons/cm², and the remainder a density of 4.1×10^{11} electrons/cm². The average density over the area would be 2.3×10^{11} . The computed force would be 1.96×10^4 dyne/cm², whereas the actual force would be $[(0.48)(0.44) + (0.52)(56)] \times 10^3 = 2.83 \times 10^4$ dyne/cm², or 43% more than inferred.

In this case, the differences in work function between the portions of the surface were small, i. e. 0.125 volts. With differences of work function of a volt or more between different portions of the surface, the inferred force of adhesion may approach only that fraction of the total force of adhesion which is represented by the fraction of the surface at which large charge transfer occurs. If the regions of small energy barrier constitute only 1/20 of the surface, and the remainder are regions of at least 0.25 eV greater barrier, the inferred force will be approximately 1/20 of that which will be measured.

2. The Manner of Break of an Adhesion Sample.

To some extent, the differences in actual adhesion which accompany the differences in charge transfer will affect the manner of the actual break when a tensile force is exerted on the sample. Initially the weak portions will come free, and as this occurs the force will be applied more and more to the portions which remain. This reduces the area actually opposing the applied force. The breaking strength is then the applied force which is equal to the sum of the individual regional forces at the regions remaining joined at that applied forces, each weighted by the area over which it extends. If the breaking apart of the weaker portions is only partial, then some forces remaining in these regions must be added to the weighted sum.

It is, however, apparent, that: 1) the sample will not break in one

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explosive rupture, but rather in a succession of partings commencing with the weaker regions and ending with the stronger ones.

1) This is what is occurring during the latter part of the half minute to a minute the tensile specimen is being stressed before break. Such separations produce little physical separation of adhesive members and therefore yield no trace on the oscilloscope.

2) As the parting of a small region cannot occur instantaneously, relaxation times should be observed. In particular, if a near-breaking force is applied to a bond, parting commences at the weaker points, and if the force remains applied, the breakings continue; as portions are broken, the remainder of the adhesive force extends over a smaller area and therefore, although resisting force per unit actual area is greater, the sum total resisting force at any time is decreased, and therefore after a finite time, the specimen may break, even though it did not originally.

3) Experimentally, it was found that the part of the break causing the observed portion of the trace occurs in less than a microsecond, and apparently in less than 1/10 microsecond. The remainder of the trace is caused by the separation of the broken halves of the sample. Therefore, the most strongly adhering portions of the adhesive which break last, break in a rapid rupture, and their separation accounts for a large charge separation, as would be expected because stronger adherence means more charge. The break takes place at a force which is essentially the sum of the forces from the most highly adherent portions of the bond.

4) If the dielectric is one of suitable resistivity, the charges remain in place, and if the applied force is removed before break, the regions which have separated will return to the metal and re-adhere. In this they will be aided by the forces on the strongest of those which have just separated; in the absence of chemical reaction, they will successively be pulled back to the interface and adhesion will be nearly that of the original specimen.

5) However, the pulling away of the adhesive temporarily leaves the surface active, and any penetration of an oxidizing or other chemically reactive atmosphere will destroy the charge pattern and produce chemical change. Therefore, if internal cracks develop, and the air penetrates, the sample will have been weakened.

E. Lateral Forces.

1. Maxwell Forces.

As stated in the text (Sec. II), the forces correspond to internal pressures, and therefore there are lateral forces equal to the adhesive forces. These lateral forces will also vary in magnitude, being greater when there are many charges per unit volume than when there are only a few.

2. Equalization of Charge.

The lateral forces on the charges will tend to drive them from regions of greater concentration into regions of smaller concentration, and iron out the discrepancy in densities. This is the origin of the diffusion term in the basic

equation. On the other hand, the charges are not all free to move inside the material, and therefore a force will be exerted on the material.

3. Internal Stresses in the Dielectric.

Stresses will therefore exist at the boundary, within the dielectric. These stresses will be in the direction from more heavily charged material to the less heavily charged. These internal stresses must be considered when the breaking behavior of the sample is examined. At the interface, the charges are neutralized in the longitudinal direction or tend to be so. The reverse is true in the lateral direction, since on either side of the interface, the regions of high charge are regions of stress laterally and no neutralizing charge can be found in the lateral direction; in the case where the work function changes greatly a positive region may be contiguous to a negative one, but this will not usually be the case. The stresses may rise to values which are more than can be supported by the material, and cracking or other failure will commence. This may be the means by which defects occur; inhomogeneities in the material will affect the concentrations of charge, and produce both mechanical and electrical stresses, the defects forming in complying with the stresses.

4. The Pattern of Adhesive on a Broken Sample.

In many cases, the broken sample shows a ridge or leaflike pattern of where the polymer adhesive joined the two halves. In between there appears to be little if any joining. Such a pattern would be expected if different portions received smaller or larger amounts of charge in the first wetting, and the electrical lateral field aided the diffusion of material into such patterns as to minimize the total free energy and reduce lateral forces so far as possible. The mechanical and electrical forces would act as a sort of guide to draw the polymer up by creep or viscous flow into the pattern, either during cure, or during the actual tensile break.

The actual patterns observed at break require further explanation than this, though, since those observed on a given sample shape are roughly alike. The effect here described is probably a small-scale effect, and the geometry of the sample, and the volume distributions of stresses suffered by the sample during cure, cooling and stressing before break, and therefore attributable to external sources must be responsible for the major overall pattern.

5. The Plane of Cleavage.

In the work of Patrick and Vaughn (33-4), it was found that "utilizing present methods, it is not possible to rupture metalorganic bonds when monolayers are deposited onto the substrate. In every case examination revealed cohesive rather than adhesive bond rupture". From the above, this would appear to be quite reasonable. Within the organic material, there would be set up lateral stresses as well as longitudinal stresses. The lateral stresses would predispose to internal cracking, or its equivalent. The adhesion to the metal surface would be the greatest at the interface, and decrease further back into the material. If there were the expected variation in cohesive forces because of the random positioning of long-chain molecules, it would appear much more likely that the summation of forces would favor a break at some point within the vicinity of the interface, than at the interface itself at which the adhesive force is the greatest. Attempts to calculate the depth into the plastic at which the break is likely to occur are restricted by the assumptions which must be made as to the cohesive forces, and since there is little clue as to their dependence on depth, qualitative pictures only are justified.

Appendix IV.

MECHANICAL PULSES AND WAVES AT SAMPLE BREAK REFLECTED IN THE MECHANICAL MEASURING SYSTEM AND THEIR OBSERVATION ON THE ELECTRICAL OSCILLOGRAPH TRACE.*

A. Observation of the Phenomenon.

1. Discontinuities in Oscillograph Traces.

In the various series of oscillograph traces photographed, there exist a number of smooth rise and decay curves of potential at break. A number of traces, however, showed a much more complex behavior. Examples of this may be seen in Figs. 29 to 36 b, of Ref. 36, WADC Technical Report 56-158. In Fig. 30 for example, a sudden rise in the curve occurring relatively instantaneously compared with the remainder of the curve is evident in curves 1, 3, and 4, and only one such sudden rise occurs. This was a mechanically nonbrittle bond, and the type of pulse is quite distinguishable from those in Fig. 35 b, and 36 b, which are largely caused by the brittleness of the polymer, which had received 96 hours' cure rather than the combination of 210 min. prepolymerization and 12 hours' cure.

Similar sudden rises were observed in the various samples broken in this work. Such phenomena are illustrated in Figs. 34 - 39 of the present report. These were observed on the Baldwin - Tate Emery tensile test machine.

2. Correlation of the Phenomena with Distribution of Adhesive at Break.

For most of the deviations of the trace pattern from smooth behavior, it was possible, at least qualitatively, to make correlation with the appearance of the adhesive on the two samples. In complex cases, the interpretation was difficult, but in the simpler cases, there was agreement with the envisioned process. Thus, the pattern shown as the fourth curve in Fig. 29 of WADC TR 56-158 corresponded to samples in which tearing started from the face of one sample, and then from that of the other sample, and then finally breaking, as indicated by the lifted portions of torn polymer on each face. (Note that the trace was taken with the "notch" on, so that the half of the picture to the left of center is traversed at ten times the speed of that at the right.)

*The main portion of this section was presented to the March 1, 1957 meeting of the American Physical Society at the University of Oklahoma. It is published in Bulletin of the American Physical Society, II, 2, 98 (1957), "Use of the Electrical Potential at the Break of an Adhesive Bond in Studying Elastic Pulses and Waves during Break." (41)

In the case of the pulses, however, it proved difficult to find patterns on the broken samples which would yield an explanation of the trace. The possibility of elastic pulses was therefore investigated.

3. Pulse Times.

Upon analysis of the times after break at which they occurred, it was found that the discontinuities occurred chiefly at times of:

- a) 220 and 440 μ sec.
- b) 360 - 380 μ sec.
- c) 900, 1800 and approx. 3600 μ sec.
- d) 1400 - 1600 μ sec.

B. Explanation of the Phenomena.

1. The Effect of a Pulse on the Trace.

If a mechanical pulse originates at break and travels down portions of the tensile machine, at some point it will reflect and return. Upon its return, it will meet the specimen as it is separating immediately after break. Except for the pulse, the potential trace would show an exponential-like decay; when the pulse arrives, it produces a sudden displacement of the sample, and if it is a rarefaction, therefore decreases the capacity of the equivalent condenser. The gradual settling back may be seen or may be lost in the continued separation of the specimens after break. This decrease of capacity, with a given charge on the specimen produces an increase of potential which takes place as rapidly as the pulse. Similarly, a condensation pulse will cause a decrease of the potential trace.

2. Time of Pulse Observation.

The times of pulse occurrence must correspond to the time necessary to travel twice the distance to the point at which reflection occurs. In the case of long pulses, there may be several reflections, or a different mechanism may be involved. Thus, an initial pulse reflected at the I-beam may give it a kick which causes it to bend upwards and in part rotate upwards on its fulcrum, and the time for the return kick will depend upon calculations other than purely speed of sound calculations.

If the times observed are roughly converted to half distances, at an average speed of sound, the first two sets yield about 1.6 and 3.2, and 2.8 feet respectively. The distance from the sample to the I-beam can be correlated with the first of these, and the 3.2 feet distance would then be considered a second multiple. As indicated in the previous paragraph, the complex mechanical construction of the tensile tester, and the lengths of the times involved make further considerations somewhat tenuous.

C. Experiments for Confirmation of Effect of Pulses.

1. Sample-Support Design.

In order to obtain pulses more easily interpretable, there were designed several sample supports, with the aim of producing a sufficiently intense pulse reflection at a predetermined distance from the sample. The sam-

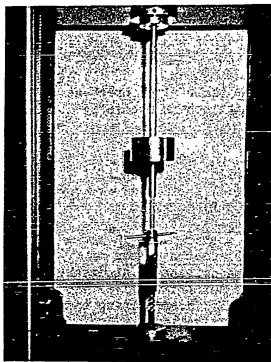


Fig. 32 Sample support system with massive weight.

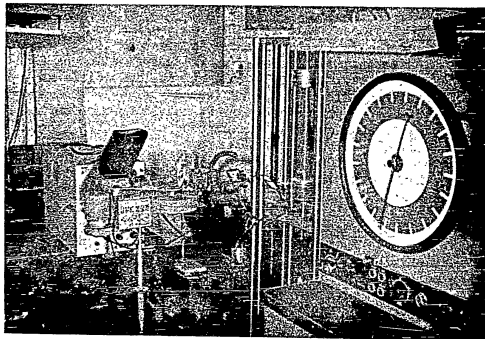


Fig. 33 Testing apparatus including tensile, electrical and vacuum equipment.

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ple supports consisted of a series of thin rods of $3/4$ " diameter, threaded at one end and tapped at the other, and one or more massive blocks of the same material. The massive blocks were so designed that the pulse would enter the mass of metal with little reflection, but would reflect from the far surface of the block and return to the sample after traversing known distances. The distances were made variable by using one or more of the thin support rods between the sample and the massive reflection block.

One such reflection plate system was made up ; its performance was not satisfactory, and the system pictured in Fig. 32 was constructed.

2. Measurements.

With the system pictured in Fig. 32, there were obtained pulses at 33 microseconds if the first thin rod only is inserted between the reflection plate and the sample, and 62 microseconds if the two were used. These values correspond to the time of travel twice along one rod or the two rods, as calculated from their length and the speed of sound in stainless steel.

3. Computations.

a. Using the Machined Reflection Plates: Aluminum Sample.

Let T be the time of travel of the pulse, L_a be the length of the aluminum through which it must pass, and L_s be the length of stainless steel through which it must go before being reflected, V_a and V_s be the speeds of sound in aluminum and steel respectively.

$$T = \frac{L_a}{V_a} + \frac{L_s}{V_s}$$

$$V_a = 16740 \text{ ft/sec} = 2.01 \times 10^5 \text{ in/sec.}$$

$$V_s = 16410 \text{ ft/sec} = 1.97 \times 10^5 \text{ in/sec.}$$

$$L_a = 1.5"$$

$$33 = \left(\frac{1.5}{2.01} \times 10^{-5} + \frac{2 L_s}{1.97} \times 10^{-5} \right) 10^6 \text{ } \mu\text{sec.}$$

$$= 7.46 + 10.02 L_s \text{ } \mu\text{sec.}$$

$$\therefore L_s = 2.55 \text{ in.}$$

$$62 = 7.46 + 10.02 L_s \text{ } \mu\text{sec.}$$

$$L_s = 5.45 \text{ in.}$$

The first length of stainless steel corresponds to the length of the first rod section, and the second one to the length of the first and second sections. Since the pulse must be assumed to go through the aluminum only once, it appears that the pulse originated at the contact between the sample, and its first metal support.

Similar results were obtained with other samples.

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b. Attempt to Apply the Calculations to Pulses in Tensile Machine.
The times of travel listed in Sec. A 1 above, of this Appendix, resulted when the regular sample holder identical to the lower one was substituted for the machined rods and reflection plates.

As an example, consider a pulse obtained at 360 microseconds with a copper sample.

$$T = \frac{L_{Cu}}{V_{Cu}} + \frac{L_{Br}}{V_{Br}} + \frac{L_s}{V_s}$$

where the subscripts Cu, Br, and S, refer to copper, brass, and steel (not stainless steel).

$$T = \frac{2(.75)}{1.40 \times 10^5} + \frac{2(1.75)}{1.38 \times 10^5} + \frac{2L_s}{1.96 \times 10^5}$$

$$L_s = \frac{T - 36}{10.02} \text{ } \mu\text{sec.}$$

If T is 360 microseconds, L is 32.4 inches, or twice the distance up to the balance (I-) beam so that this would correspond to the travel of a pulse twice up and twice back.

D. Conclusions.

The pulses originating during the break of the specimen travel and are reflected, because of the nature of the support during tensile stressing. These are reflected at various places in the test machine and are observable on the trace by the separating condenser effect; a quasi-instantaneous separation of the halves of the specimen causes a quasi-instantaneous increase of potential across the condenser, i. e. a sudden displacement of the trace, which is characteristically recognizable. This may be used to study the effects occurring at break. Their use to analyze the more complex sets of return pulses due to and within the structure of the tensile machine does not yield unambiguous data, at least without a considerably more detailed analysis of the elastic responses possible within the machine.

Some success was had in matching the rise of the trace with the computed elastic response of the system, which would indicate that elastic waves occurring during break could also be studied. However, rigidly accurate matching of input and output wave forms of the oscillograph would be necessary here to avoid introducing extraneous material, and the time and effort which would have been involved in extending this to detailed rather than rough studies of waves were not appropriate to the subject matter of the contract. Therefore the work was carried only far enough to demonstrate the reality of the effect.

The possibility, however, has been shown, of using the oscilloscope trace which results from the electrical behavior at the break of an adhesive bond to study transient mechanical effects occurring during the microsecond or less of actual break and the milliseconds immediately following this before

separation has become measurable by the usual method. Since strain gage measurements do not yield accurate results in this region, this method of study offers practical possibilities. The most favorable time for study of the mechanical effects is when the trace is descending from its peak, which constitutes some 80% or so of the time in which phenomena related to the break, rather than the subsequent equilibrium, are dominant.

Figure 34

Aluminum - PMMA

Showing wave maxima at 67 and 101 useconds and minima at 52, 87, 128 useconds giving a period of 35 useconds (see appendix on Reflection Waves). Charge seen by circuit (by integration under the curve) is 18.5 esu/cm^2 .

Figure 34

Copper - PMMA

Showing a reflection wave at 1680 useconds using coaxial cable probe.

Figure 34

Aluminum - PMMA

Showing a reflection wave at 220 useconds. Polymer stripped from bottom metal face, giving a negative trace for negatively charged polymer.

Figure 34

Aluminum - Polystyrene

Showing similarity to traces obtained from Aluminum - PMMA with the same sign of charge on polymer. A coaxial cable probe was used which had a large rise time. Initial portion of rising voltage is faintly visible.

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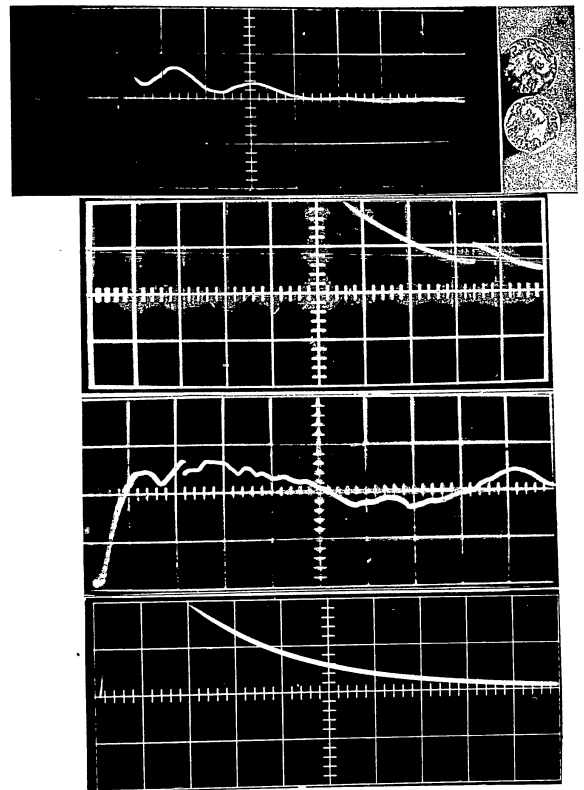


Fig. 34

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Figure 35

Polished Copper - PMMA - Ground Copper

Shows multiple reflection displacements of the curve. Time origin of trace is not determined, the displacements coming at 210, 370, and possibly at 440 microseconds from start of sweep.

Figure 35

U 10 - Aluminum - PMMA

Showing multiple reflection wave displacements at 190 and 300 microseconds. Integrated charge was 2.22 esu.

Figure 35

V 11 - Copper - PMMA

About one half the polymer broke off the top metal and half off the bottom metal resulting in the large positive and negative portions of the curve. Note reflection wave at 800 microseconds. Integrated charge density is 2.9 esu/cm².

Figure 35

W 19 - Nickel - PMMA

Shows similarity to V 11 in its trace and alternate stripping of polymer from metal. Reflection wave displacement at 280 microseconds.

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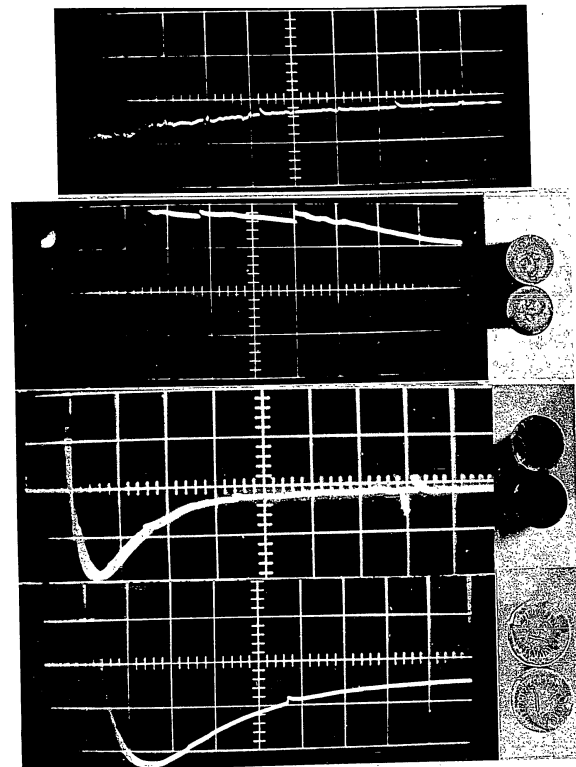


Fig. 35

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Figure 36

V-9 Copper - PMMA

The polymer stripped alternately from the two metal faces as shown, thereby giving a trace which also goes negative.

Figure 36

U-15 Nickel - PMMA

Showing stripping predominantly from the top surface and giving an integrated charge value of 24.7 esu/cm^2 . A predominant reflection wave at 350 $\mu\text{seconds}$ is shown.

Figure 36

V-014 Nickel - PMMA

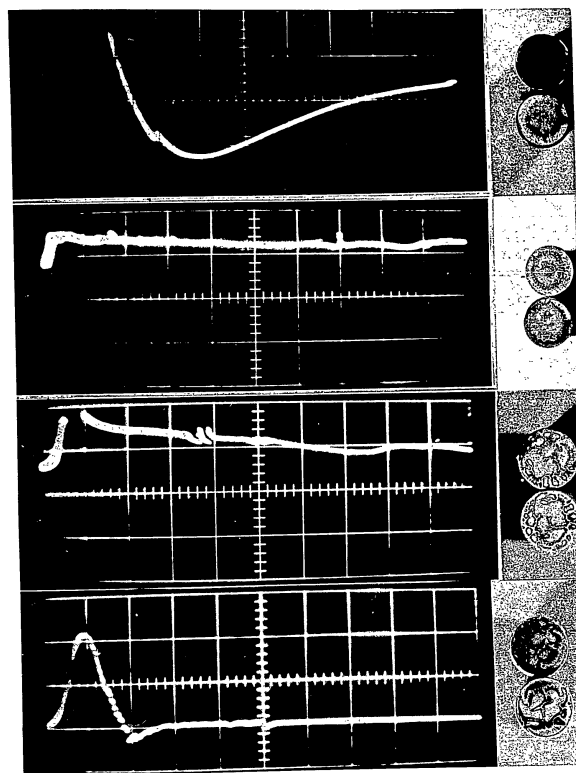
A cathode follower probe was used.

Figure 36

X-20 Nickel - PMMA

The bond strength was 700 lb/cm^2 for an area of 0.537 cm^2 .

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Fig. 36
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Figure 37

X 8 - Copper - PMMA

Breaking strength of 370 lb. in a vacuum of .02 mm. Hg. Integrated charge density is 4.53 esu/cm².

Figure 37

U 018 - Copper - PMMA

Fairly well defined polymer ring. A reflection wave displacement is seen at 370 microseconds. Integrated charge density is 21.9 esu/cm².

Figure 37

X 21 - Nickel - PMMA

A fairly well defined ring giving a breaking strength of 460 lb. for an area of .570 cm². Pulled in .09 mm. pressure.

Figure 37

V 020 - Aluminum - PMMA

Polymer layer broke 90% from the top metal member giving an all positive trace. Reflection wave displacement at 120 microseconds. Integrated charge density is approximately 11 esu/cm².

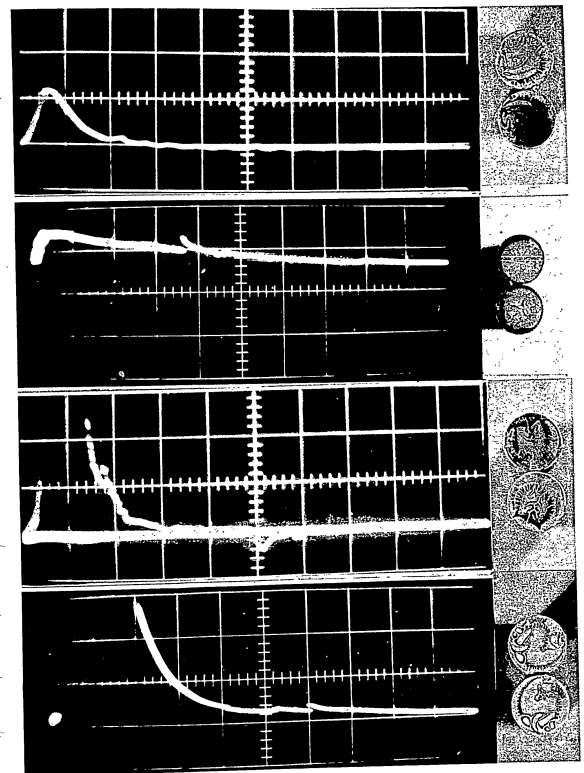


Fig. 37

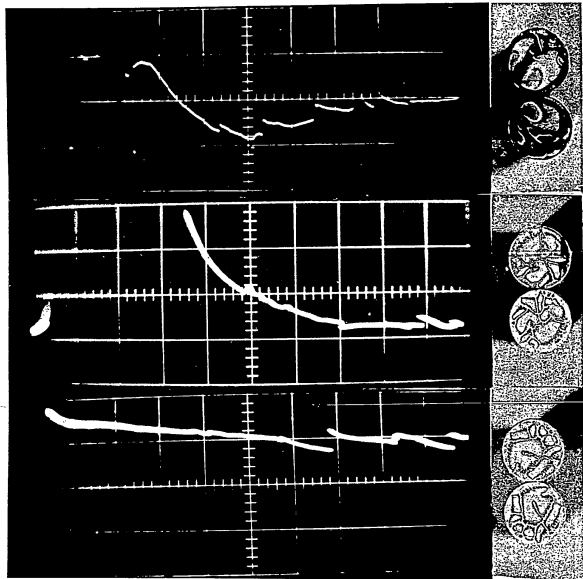


Fig. 38

- Trace 1: W 4 - Copper - PMMA. Metal diffused through the polymer. Reflection wave displacements are at 220, 270, 325, 370, 395 and 435; some of these fall in frequently observed ranges.
- Trace 2: V 019 - Aluminum - PMMA. Shows a polymer layer where the fern-like pattern is at a minimum. It is frequently observed that this pattern is more pronounced on copper and nickel than on aluminum. Reflection wave displacements at 350 and 440 μ seconds. Integrated charge approximately 5 esu.
- Trace 3: V 015 - Aluminum - PMMA. Multiple reflection wave displacements at 380, 415 and 480 μ seconds.

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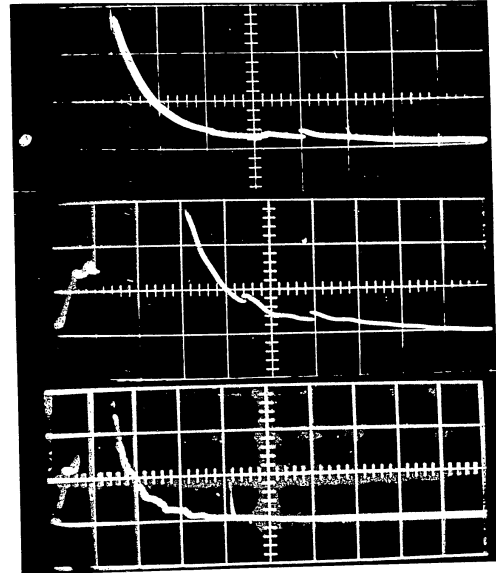


Fig. 39

- Trace 1: V 020 - Aluminum - PMMA. Reflection wave displacement at 300 μ seconds. Integrated charge is approximately 5.9 esu.
- Trace 2: X 010 - Aluminum - PMMA. Pulled at 0.04 mm. pressure with an integrated charge value of approximately 4.1 esu. Reflection wave displacements at 44 and 60 μ seconds are probably caused by the vacuum chamber.
- Trace 3: V 20 - Copper - PMMA. Metal diffused through polymer. Pulled at 0.08 mm. pressure, showing an integrated charge of 17.0 esu.

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